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Anomalous Pressures and Vibrations in Gas Explosions. Determination of the Dissociation Energy $2H_2O \rightleftharpoons 2OH + H_2$[1]

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Using thermodynamic functions of gases derived from band spectra, calculations have been made of theoretical explosion pressures in mixtures of hydrogen and oxygen containing various inert gases which are compared with explosion pressures observed experimentally by different investigators. Details of methods of calculation are given. In carefully dried mixtures of hydrogen and oxygen with excess hydrogen, the observed pressures are too low. This effect is eliminated by the addition of small amounts of water vapor to the original mixture which, according to an hypothesis advanced by Wohl and von Elbe, quenches the luminescence from OH radicals formed in the flame front. In mixtures containing excess oxygen or nitrogen the observed pressures are too high. The existence of a lag in the excitation of the vibrational energy levels of oxygen and nitrogen during the explosion period, as advanced by Wohl and Magat, is offered as explanation. The excitation lag is greater in oxygen than in nitrogen. Explosions of mixtures of gaseous ozone diluted with oxygen do not show this effect, even though the explosion time for approximately the same explosion temperature hardly differs from that of a hydrogen-oxygen explosion which shows the excitation lag. This is explained on the assumption that there is no appreciable lag in the transfer of vibrational energy between like molecules. A similar excitation lag apparently does not exist in H_2O and H_2. The phenomenon of time-variable heat capacities within the duration of an explosion may be used to explain the intense audible vibrations observed by the authors and others on exploding slow burning lean mixtures of hydrogen with air or oxygen within a certain concentration range. The possible bearing of this effect on the phenomenon of engine knock is mentioned. Explosions were made of mixtures of hydrogen and oxygen with helium as inert gas, which are free from both anomalous effects mentioned above and the energy of dissociation of the reaction $2H_2O \rightleftharpoons 2OH + H_2$ was calculated from the data obtained with the aid of accurate thermodynamic functions of the gases involved. The average of the results of six explosions was found to be 126,000±2000 calories per 2 moles of H_2O. From this value one obtains

$$H_2O \rightleftharpoons H + OH - (114{,}400 \pm 1000) \text{ calories}$$

$$OH \rightleftharpoons H + O \quad - (104{,}160 \pm 1000) \text{ calories.}$$

THE explosion method has been used considerably during the past 25 years for the determination of heat capacities and dissociation data without knowing precisely how much reliance was to be placed on the use of measured explosion pressures for such purposes. Because of the recent exact evaluation of thermodynamic functions of gases from band spectra one may calculate accurately the pressures which should be developed provided the explosion is adiabatic and provided complete dissociation equilibria and equilibria among the different quantum states are established. Since the experimental data on hydrogen-oxygen explosions are secured by agreement of the observations of various independent investigators this procedure of comparing calculated with observed pressures must bring to light any existing anomaly.

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It has been usual to assume that the observed maximum pressure corresponds to a condition of equalized temperature throughout the vessel. In reality there is a temperature gradient rising inward from the wall to the point of ignition at the center. In the thermodynamic calculation of explosion pressures the effect of this temperature gradient must be corrected for. The pressure for the temperature gradient system is lower than that for the equalized temperature system by an amount (0.1 to 1 percent)[4] which varies with the composition of the explosive mixture.

The writers have carried out the calculations for the existing reliable data[5, 6, 7, 8] on explosions of mixtures of hydrogen and oxygen containing various inert gases employing reliable spectroscopic data[9] on dissociation constants and energy content of the gases involved.

Method of Calculation

The method of calculation for the different types of explosions is basically the same as that of Wohl and co-workers,[10] with the addition that the theoretical explosion pressure is corrected for the effect of the temperature gradient in the exploded gas as outlined in a previous paper.[4]

In the calculations which follow, the unknown quantity sought is $\acute{P}e$(calc.), the pressure for the unequalized temperature state actually existing at the end of an explosion, which is to be compared with $\acute{P}e$(obs.), the observed explosion pressure. This is the most direct way of comparing experiment with theory.

Since H_2O dissociates in two different ways, namely,

$$\text{I. } 2H_2+O_2 \rightleftharpoons 2H_2O+114{,}222$$

$$\text{II. } 2OH+H_2 \rightleftharpoons 2H_2O+126{,}000^{11}$$

and the dissociations are affected differently by hydrogen and oxygen, the method of calculation differs slightly with the type of gas mixture, that is, containing

Case 1. Large excess of hydrogen.

Case 2. Small excess of hydrogen or stoichiometric mixture.

Case 3. Excess oxygen.

Case 1. Explosions with large excess of hydrogen and with or without inert gases

The inert gases may be nitrogen, argon and water vapor. At explosion temperatures nitrogen will neither dissociate nor react with hydrogen appreciably, but the dissociation of hydrogen must be considered. For the combustion of 1 mole of hydrogen at room temperature,

$$\frac{57{,}501}{T\bar{e}-Ti}=(1+m_{H_2O})\left|CvD_{(H_2O)}\right|_{Ti}^{T\bar{e}}$$

$$+m_{H_2}\left|CvD_{(H_2)}\right|_{Ti}^{T\bar{e}}+m_{N_2,A}\left|CvD_{(N_2,A)}\right|_{Ti}^{T\bar{e}}, \quad (1)$$

where 57,501 is the heat of combustion of 1 mole of ordinary hydrogen gas, at constant volume and room temperature. This value has been determined for 298.1°K, but may be assumed constant for a small temperature range. $T\bar{e}$ is the temperature which would exist at the end of an explosion if the temperature were equalized throughout the vessel without loss of heat to the wall. Ti is the temperature of the gas mixture before explosion. m_{H_2O}, m_{H_2}, etc., are the moles of the indicated gases in the burned mixture per mole of H_2O formed disregarding all dissociations, that is, per 1/2 mole of O_2 originally

[4] Lewis and von Elbe, J. Chem. Phys. **2**, 659 (1934).

[5] Pier, Zeits. f. Elektrochemie **15**, 536 (1909); Bjerrum, Zeits. f. physik. Chemie **79**, 513 (1912); **81**, 281 (1912).

[6] Wohl and von Elbe, Zeits. f. physik. Chemie **B5**, 241 (1929).

[7] Wohl and Magat, Zeits. f. physik. Chemie **B19**, 536 (1932).

[8] Also supplementary explosions by the authors contained in this paper.

[9] Free energy and energy content of water vapor. Gordon, J. Chem. Phys. **2**, 65, 549 (1934).

Free energy and dissociation constants of hydrogen. Giauque, J. Am. Chem. Soc. **52**, 4816 (1930). See also Davis and Johnston, ibid. **56**, 1045 (1934), for slight corrections above 2000°.

Energy content of hydrogen. Davis and Johnston, J. Am. Chem. Soc. **56**, 1045 (1934).

Free energy, dissociation constants and energy content of oxygen. Johnston and Walker, J. Am. Chem. Soc. **55**, 172, 187 (1933). Lewis and von Elbe's (ibid. **55**, 507, 511, 1933) values of the dissociation constants and energy content include the contribution of the oxygen $^1\Delta$ level. The free energy of Johnston and Walker should be corrected for the $^1\Delta$ level.

Constant of equilibrium of $NO \rightleftharpoons 1/2\ N_2+1/2\ O_2$. Giauque and Clayton, J. Am. Chem. Soc. **55**, 4875 (1933).

Energy content of nitrogen. Johnston and Davis, J. Am. Chem. Soc. **56**, 271 (1934).

Free energy of OH. Johnston and Dawson, J. Am. Chem. Soc. **55**, 2744 (1933).

Heat of formation of H_2O from H_2 and O_2. Rossini, Bur. Standards J. Research **6**, 1 (1931).

[10] See reference 7 for other references.

[11] See below.

present. $CvD_{(H_2O)}\big|_{Ti}^{T\bar{e}}$, etc., are the heat capacities between Ti and $T\bar{e}$ of the gases indicated including the contribution of dissociation to the heat effect.

For large excess of hydrogen, dissociation I may be neglected. Thus

$$\left|CvD_{(H_2O)}\right|_{Ti}^{T\bar{e}} = \left|Cv_{(H_2O)}\right|_{Ti}^{T\bar{e}} + D_{II} \qquad (2a)$$

and

$$\left|CvD_{(H_2)}\right|_{Ti}^{T\bar{e}} = \left|Cv_{(H_2)}\right|_{Ti}^{T\bar{e}} + D_{H_2}, \qquad (2b)$$

$$D_{II} = (\Delta E^\circ_{T\bar{e}})_{II} x_{II}/(T\bar{e}-Ti) \qquad (3a)$$

and

$$D_{H_2} = (\Delta E^\circ_{T\bar{e}})_{H_2} x_{H_2}/(T\bar{e}-Ti), \qquad (3b)$$

where $(\Delta E^\circ_{T\bar{e}})_{II}$ and $(\Delta E^\circ_{T\bar{e}})_{H_2}$ are the energies of dissociation of H_2O and H_2, respectively, and x_I and x_{H_2} are the corresponding degrees of dissociation.

Pe, the explosion pressure for the equalized temperature state is calculated from the gas law.

$$Pe = [(T\bar{e}/Ti)Pi(1+\Sigma m)/(1.5+\Sigma m)] + \Delta Pe, \qquad (4)$$

where ΔPe is the excess of pressure due to increase in the number of molecules caused by dissociation

$$\Delta Pe = 0.5(p_{OH} + p_H), \qquad (5)$$

where p_{OH} and p_H are the partial pressures of OH and H existing in dissociation equilibrium.

The dissociation equilibria are determined by the constants

$$K_{pII} = p_{H_2} p_{OH}^2/p_{H_2O}^2, \qquad (6)$$

$$K_{pH_2} = p_H^2/p_{H_2}, \qquad (7)$$

p_{H_2O}, p_{H_2}, p_{OH}, and p_H are given by

$$p_{H_2O} = (T\bar{e}/Ti)[pi_{H_2}/(1+m_{H_2}) + pi_{H_2O}](1-x_{II}), \qquad (8)$$

$$p_{H_2} = (T\bar{e}/Ti)[pi_{H_2} m_{H_2}/(1+m_{H_2}) + \{pi_{H_2}/(1+m_{H_2}) + pi_{H_2O}\}0.5x_{II}][1-x_{H_2}], \qquad (9)$$

$$p_{OH} = (T\bar{e}/Ti)[pi_{H_2}/(1+m_{H_2}) + pi_{H_2O}]x_{II}, \qquad (10)$$

$$p_H = 2(T\bar{e}/Ti)[pi_{H_2} m_{H_2}/(1+m_{H_2}) + \{pi_{H_2}/(1+m_{H_2}) + pi_{H_2O}\}0.5x_{II}]x_{H_2}, \qquad (11)$$

where pi_{H_2} and pi_{H_2O} are the partial pressures of these gases in the unburned mixture at Ti.

The value of Pe is obtained by the method of trial and error. A temperature $T\bar{e}$ is estimated and with the aid of the known values of heat capacities and dissociation constants,[9] x_{II} and x_{H_2} and consequently D_{II} and D_{H_2} are evaluated. If Eq. (1) is not fulfilled a new value of $T\bar{e}$ is chosen and the calculation repeated.

The ratio $Pe/\acute{P}e$ is determined separately from the relation[4]

$$Pe/\acute{P}e = T\bar{e}(1+\bar{x})/\int_0^1 Te(1+x)dn, \qquad (12)$$

$(1+\bar{x})$ is the ratio of the number of molecules in the burned mixture in the dissociation equilibrium state and the undissociated state for the temperature $T\bar{e}$. Therefore

$$\bar{x} = \Delta Pe/(Pe-\Delta Pe) = [(1+m_{H_2O})0.5x_{II} + m_{H_2}x_{H_2}]/(1+\Sigma m). \qquad (13)$$

The corresponding symbols for the unequalized temperature state are within the integral of Eq. (12) which is to be taken over all elementary fractions dn of the burned gas. n varies from 0 to 1. One first obtains a curve of $\Sigma m\left|CvD\right|_0^{Te} \times Te$ as a function of n as outlined previously.[4] The area under this curve equals $\Sigma m\left|CvD\right|_0^{T\bar{e}} \times T\bar{e}$. This enables one to obtain Te and $(1+x)$ as functions of n and also $T\bar{e}$ and $(1+\bar{x})$. For calculation of the ratio $Pe/\acute{P}e$ it is preferable to use the value of $T\bar{e}$ determined from the above area rather than by Eqs. (1) to (11), in order that slight inaccuracies in the $\Sigma m\left|CvD\right|_0^{Te} \times Te$ *versus* n curve shall not enter into the $Pe/\acute{P}e$ ratio. In any case both values of $T\bar{e}$ are very close to each other.

Case 2. Explosions with small excess of hydrogen or of stoichiometric mixture and with or without inert gases

In this case one must consider both dissociations I and II, and in the presence of nitrogen the formation of NO, namely, $2NO = N_2 + O_2 + 42{,}800$. It is advantageous to combine all dissociation terms into a single term ΣmD, so that Eq. (1) now reads:

$$\frac{57{,}501}{T\bar{e}-Ti}=(1+m_{H_2O})\left|Cv_{(H_2O)}\right|_{Ti}^{T\bar{e}}+m_{H_2}\left|Cv_{(H_2)}\right|_{Ti}^{T\bar{e}}$$

$$+m_{N_2,A}\left|Cv_{(N_2,A)}\right|_{Ti}^{T\bar{e}}+\Sigma mD. \quad (14)$$

Let m_{OH}, m_H, m_O and m_{NO} represent the number of moles of the indicated gases at equilibrium per mole of H_2O formed for complete reaction, that is per 1/2 mole of O_2 originally present.

To bring the gases to equilibrium first allow a sufficient amount of H_2O to dissociate into H_2 and O_2 and then let H_2 and O_2 combine according to

$$\text{III.}\quad H_2+O_2=2OH-11{,}800$$

until equilibrium is reached. Then

$$\Sigma mD=(0.5/(T\bar{e}-Ti))[(\Delta E^\circ_{T\bar{e}})_I(m_{OH}+2m_{O_2}$$
$$+m_O+m_{NO})+(\Delta E^\circ_{T\bar{e}})_{III}m_{OH}+(\Delta E^\circ_{T\bar{e}})_{H_2}m_H$$
$$+(\Delta E^\circ_{T\bar{e}})_{O_2}m_O+(\Delta E^\circ_{T\bar{e}})_{NO}m_{NO}]. \quad (15)$$

The following equilibria are to be considered in addition to Eqs. (6) and (7)

$$K_{pI}=p_{H_2}{}^2p_O/p_{H_2O}{}^2; \quad (16)$$

$$K_{pO_2}=p_O{}^2/p_{O_2}; \quad (17)$$

$$K_{pNO}=p_{NO}{}^2/p_{N_2}p_{O_2}, \quad (18)$$

m_{OH}, m_H, etc., are expressed by the following equations

$$m_{OH,\,H,\,O,\,NO}=(p_{OH,\,H,\,O,\,NO}/2pi_{(O_2)})Ti/T\bar{e}, \quad (19)$$

where pi_{O_2} is the partial pressure of O_2 in the unburned mixture at the temperature Ti.

Values of p_{H_2}, p_{H_2O} and p_{NO} are affected by the multiple dissociations and are given by

$$p_{H_2}=(pi_{H_2}-2pi_{O_2})T\bar{e}/Ti+0.5p_{OH}$$
$$+2p_{O_2}+p_{NO}+p_O-0.5p_H, \quad (20)$$

$$p_{H_2O}=(2pi_{O_2}+pi_{H_2O})T\bar{e}/Ti-p_{OH}$$
$$-2p_{O_2}-p_{NO}-p_O, \quad (21)$$

$$p_{N_2}=pi_{N_2}T\bar{e}/Ti-0.5p_{NO}. \quad (22)$$

Pe is obtained from Eq. (4), except that ΔPe is now

$$\Delta Pe=0.5(p_{OH}+p_H)+p_{O_2}. \quad (23)$$

Case 3. Explosions with excess oxygen and with or without inert gases

In this case the same dissociation equilibria as in Case 2 are considered. Eq. (19) changes to

$$m_{OH,\,N,\,O,\,NO}=(p_{OH,\,N,\,O,\,NO}/pi_{(H_2)})Ti/T\bar{e}. \quad (24)$$

The term $m_{O_2}|Cv_{O_2}|_{Ti}^{T\bar{e}}$ is substituted for the H_2 term in Eq. (14). In Eq. (15) $(\Delta E^\circ_{T\bar{e}})_I$ is multiplied by $(0.5m_{OH}+m_{H_2}+0.5m_H)$.

The partial pressures of the various gases to be used in the equilibrium equations now read:

$$p_{H_2O}=(pi_{H_2}+pi_{H_2O})T\bar{e}/Ti-0.5p_{OH}$$
$$-p_{H_2}-0.5p_H, \quad (25)$$

$$p_{O_2}=(pi_{O_2}-0.5pi_{H_2})T\bar{e}/Ti-0.25p_{OH}$$
$$-0.5p_{NO}-0.5p_O+0.5p_{H_2}+0.25p_H, \quad (26)$$

$$p_{N_2}=pi_{N_2}T\bar{e}/Ti-0.5p_{NO}. \quad (27)$$

Tables I to IV contain the results of the calculations.

For most groups of experiments the original values of Ti and Pi have been adjusted slightly to a common pressure of 760 mm Hg and a common temperature, in most cases 291°K. This necessitates a slight correction of the observed explosion pressure, which for small changes of Pi and Ti is accomplished by the relation

$$\Delta Pe=(760-Pi)Pe/Pi-[(291-Ti)/Ti]$$
$$\times[Pe-Pi(1+\Sigma m)/(1.5+\Sigma m)]. \quad (28)$$

The agreement between the calculated and observed explosion pressures of the first group in Table I is complete, the average deviation for 15 "argon" experiments being +0.07 percent, that is, zero. The small systematic deviation (−0.61 percent) in the excess hydrogen explosions is accounted for by heat losses due especially to heat conducted through the ignition rod which is in contact with hot gas during the explosion. Such losses have been found experimentally by Wohl and Magat for these mixtures of high heat conductivity, but not for excess oxygen mixtures of low conductivity.

The value used for the energy of the dissociation reaction $2OH+H_2\rightleftharpoons 2H_2O$ is 126,000 calories, which was obtained from explosions (described later) of mixtures of hydrogen and oxygen con-

TABLE I. *Hydrogen-oxygen explosions with excess hydrogen and argon and water vapor. Comparison of* $\bar{P}e_{\text{calc.}}$ *and* $\bar{P}e_{\text{obs.}}$ $Pi = 760$ mm Hg.

Author	Explosion No.	m_{H_2O}	m_{H_2}	m_A	Ti °K	$T\bar{e}$ °K	$Cv_{Ti(H_2O)}^{T\bar{e}}$	$Cv_{Ti(H_2)}^{T\bar{e}}$	D_{II}	D_{H_2}	$Pe_{\text{calc.}}$ mm Hg	$\bar{P}e_{\text{calc.}}$ mm Hg	$\bar{P}e_{\text{obs.}}$ mm Hg	% difference
Pier	138	0.169	0.297	7.23	291	2041	8.21	5.46	0.043	0.163	5041	5009	5015	+0.12
do.	135	.166	.240	7.30	291	2047	8.22	5.46	.053	.189	5055	5023	5045	+0.44
do.	150	.140	.987	5.27	291	2153	8.33	5.51	.048	.164	5270	5236	5274	+0.73
do.	149	.123	.771	4.40	291	2381	8.53	5.60	.180	.385	5769	5731	5735	+0.07
do.	147	.126	.776	4.31	291	2392	8.56	5.61	.187	.395	5789	5751	5760	+0.16
do.	148	.119	.685	4.25	291	2440	8.60	5.63	.262	.511	5897	5858	5853	−0.09
do.	146	.115	.575	3.57	291	2600	8.75	5.69	.546	.926	6232	6188	6196	+0.13
do.	145	.114	.571	3.54	291	2613	8.76	5.70	.571	.976	6247	6203	6210	+0.11
do.	144	.113	.546	3.52	291	2627	8.77	5.71	.604	1.03	6285	6240	6240	0.00
do.	155	1.033	.401	4.803	326	2048	8.28	5.47	.050	0.120	4468	4449	4481	+0.72
do.	152	0.877	.677	3.254	326	2259	8.47	5.57	.101	.247	4852	4828	4823	−0.10
do.	151	.830	.627	3.078	326	2325	8.53	5.60	.150	.337	4979	4953	4944	−0.18
do.	153	.835	.523	3.095	326	2348	8.55	5.61	.180	.430	5058	5032	4994	−0.75
Wohl & von Elbe	51	.118	.284	4.837	291	2469	8.62	5.65	.441	.892	5984	5945	5926	−0.32
do.	52	.103	.379	3.491	291	2672	8.82	5.73	1.060	1.730	6372	6327	(6406)*	(+1.25)
													Average	+0.07
Pier	166	0.101	4.057	—	291	2112	8.29	5.49	0.015	0.045	5030	5017	5012	−0.10
do.	167	.092	3.398	—	291	2299	8.47	5.57	.036	.118	5412	5398	5384	−0.26
do.	168	.086	2.683	—	291	2533	8.69	5.67	.160	.300	5872	5852	5821	−0.53
Wohl & Magat	31	.121	3.392	—	291	2291	8.46	5.56	.034	.110	5395	5381	5340	−0.76
do.	37	.009	3.461	—	291	2320	8.50	5.58	.050	.123	5458	5443	5420	−0.42
do.	28	.123	3.007	—	291	2408	8.57	5.61	.080	.177	5629	5613	5582	−0.55
do.	32	.111	2.924	—	291	2441	8.60	5.63	.100	.200	5695	5678	5625	−0.93
do.	36	.029	3.019	—	291	2449	8.61	5.64	.108	.212	5716	5699	5680	−0.31
do.	29	.108	2.610	—	291	2548	8.70	5.68	.173	.310	5901	5881	5842	−0.66
do.	38	.008	2.723	—	291	2558	8.71	5.69	.183	.330	5939	5919	5845	−1.26
do.	30	.025	2.657	—	291	2574	8.73	5.69	.195	.350	5951	5940	5885	−0.93
													Average	−0.61

* Experimentally unreliable.

TABLE II. *Hydrogen-oxygen explosions (dry) with excess hydrogen. Comparison of* $\bar{P}e_{\text{calc.}}$ *and* $\bar{P}e_{\text{obs.}}$. $Pi = 760$ mm Hg, $Ti = 291$°K.

Author	Explosion No.	m_{H_2}	$T\bar{e}$ °K	$Cv_{Ti(H_2O)}^{T\bar{e}}$	$Cv_{Ti(H_2)}^{T\bar{e}}$	D_{II}	D_{H_2}	$Pe_{\text{calc.}}$ mm Hg	$\bar{P}e_{\text{calc.}}$ mm Hg	$\bar{P}e_{\text{obs.}}$ mm Hg	% difference
Bjerrum	110	3.260	2387	8.55	5.60	0.075	0.161	5595	5579	5485	−1.68
Wohl and von Elbe	47	3.876	2202	8.38	5.53	.024	.069	5525	5512	5100	−2.03
do.	49	3.924	2188	8.36	5.52	.024	.066	5194	5181	5090	−1.75
do.	43	3.678	2260	8.42	5.56	.037	.094	5343	5329	5235	−1.77
do.	44	3.650	2268	8.43	5.56	.040	.094	5357	5343	5242	−1.90
do.	45	2.726	2564	8.72	5.68	.180	.330	5941	5921	5808	−1.92
do.	46	2.719	2566	8.72	5.68	.180	.330	5946	5926	5810	−1.97
Wohl and Magat	34	3.779	2231	8.40	5.54	.037	.081	5282	5268	5166	−1.93
do.	27	3.500	2301	8.46	5.57	.048	.112	5424	5410	5258	−2.87
do.	33	3.324	2368	8.54	5.60	.069	.149	5556	5541	5420	−2.18
										Average	−2.00

taining a slight excess of oxygen, and helium and water vapor as inert gases. The results tabulated in Table I are not materially affected by an uncertainty in this energy value because, due to excess of hydrogen, the water dissociation is small.

In excess hydrogen explosions Wohl and von Elbe[6] found that the absence of water vapor in the original mixture caused a marked lowering of the explosion pressure. This is confirmed by reconsideration of early experiments of Bjerrum[5] and later by the work of Wohl and Magat[7] and Lewis and von Elbe.[12] The results are given in Table II. The average deviation of 10 explosions is −2.00 percent.

Quite the opposite effect is observed in the type of explosion listed in Table III. Here the experimental pressures are too high, more pronounced in the excess oxygen (average deviation +1.22 percent for 6 explosions) than in the excess nitrogen explosions (average deviation +0.79 percent for 8 explosions). Since the results of different authors agree within the limits of error the effect appears to be well substantiated. The cause of the effect was attributed by Wohl and Magat to a lag in the excitation of the vibrational energy levels in oxygen and nitrogen

[12] Reference 4, and Table IV, this paper.

TABLE III. *Hydrogen-oxygen explosions with excess oxygen and water vapor, and excess hydrogen and nitrogen and water vapor. Comparison of $\acute{P}e_{calc.}$ and $\acute{P}e_{obs.}$ $Pi = 760$ mm Hg, $Ti = 291°K$.*

Author	Explosion No.	m_{O_2}	m_{H_2O}	m_{N_2}	$T\bar{e}$ °K	$Cv_{T\bar{e}\,Ti(H_2O)}$	$Cv_{T\bar{e}\,Ti(O_2)}$	ΣmD	$Pe_{calc.}$ mm Hg	$\acute{P}e_{calc.}$ mm Hg	$\acute{P}e_{obs.}$ mm Hg	% difference
Wohl & Magat	71	2.817	0.090	0.039	2251	8.41	6.50	1.61	5246	5238	5314	+1.45
Lewis & von Elbe	2.1	2.820	.091	.044	2247	8.41	6.50	1.60	5237	5229	5277	+0.91
Wohl & Magat	72	2.900	.095	.041	2221	8.39	6.49	1.52	5187	5180	5264	+1.62
Lewis & von Elbe	2.2	2.897	.094	.045	2221	8.39	6.49	1.52	5187	5180	5235	+1.06
Wohl & Magat	70	3.044	.096	.042	2180	8.35	6.47	1.37	5106	5099	5140	+0.81
Lewis & von Elbe	2.3	3.045	.097	.046	2176	8.35	6.47	1.36	5097	5090	5165	+1.47
											Average	+1.22

Author	Explosion No.	m_{H_2O}	m_{H_2}	m_{N_2}	Ti °K	$T\bar{e}$ °K	$Cv_{T\bar{e}\,Ti(H_2O)}$	$Cv_{T\bar{e}\,Ti(H_2)}$	D_{II}	D_{H_2}	$Cv_{T\bar{e}\,Ti(N_2)}$	$Pe_{calc.}$ mm Hg	$\acute{P}e_{calc.}$ mm Hg	$\acute{P}e_{obs.}$ mm Hg	% difference
Pier	158	0.141	0.476	5.806	291	1589	7.62	5.26	0	0	5.70	3889	3885	3892	+0.18
do.	159	.130	.546	4.799	291	1744	7.83	5.33	0	0	5.79	4229	4224	4282	+1.38
do.	160	.105	.517	3.718	291	1993	8.14	5.44	0.0185	0.068	5.90	4761	4755	4837	+1.73
do.	161	.096	.443	3.186	291	2163	8.33	5.52	.061	.168	5.97	5111	5102	5175	+1.43
do.	162	.086	.366	2.519	291	2402	8.56	5.62	.232	.496	6.05	5584	5572	5614	+0.75
do.	163	.077	.434	1.894	291	2595	8.76	5.70	.471	.806	6.11	5964	5949	5940	−0.15
do.	157	1.003	.952	3.966	326	1653	7.74	5.30	0	0	5.76	3593	3591	3610	+0.53
do.	156	0.636	.356	1.984	326	2347	8.55	5.61	0.18	0.40	6.05	4867	4860	4869	+0.19
														Average	+0.79

TABLE IV. *Hydrogen-oxygen explosions (dry)—Miscellaneous mixtures. Comparison of $\acute{P}e_{calc.}$ and $\acute{P}e_{obs.}$*

Author	Explosion No.	m_{H_2}	m_{O_2}	m_{N_2}	m_A	Ti °K	Pi mm Hg	$T\bar{e}$ °K	$Cv_{T\bar{e}\,Ti(H_2O)}$	$Cv_{T\bar{e}\,Ti(O_2)}$	$Cv_{T\bar{e}\,Ti(H_2)}$	D_{H_2O}	D_{H_2}	$Cv_{T\bar{e}\,Ti(N_2)}$	$Pe_{calc.}$ mm Hg	$\acute{P}e_{calc.}$ mm Hg	$\acute{P}e_{obs.}$ mm Hg	% difference
Lewis & von Elbe	1.5	2.587	—	1.868	0.024	294.6	717.5	2013	8.17	—	5.45	0.010	0.034	5.92	4493	4484	4409	−1.67
do.	1.3	0.125	—	1.868	.024	294.3	717.5	2735	8.91	—	5.76	ΣmD 2.37		6.18	5799	5780	5806	+0.45
do.	1.2	—	0.326	3.127	.040	295.8	717.0	2187	8.36	6.48	—	ΣmD 1.12		5.98	4782	4773	4762	−0.23
do.	2.6	—	3.452	0.048	—	292.7	757.0	2097	8.28	6.44	—	ΣmD 1.06		5.95	4894	4888	4924	+0.74

molecules. That such a lag exists has been shown by the work of a number of investigators.[13] Explosion experiments therefore would seem to offer a rather novel approach to this field of study.

While the explosion times are too short to allow complete excitation of the vibrational states of oxygen and nitrogen they seem to be sufficient to do so for water vapor and hydrogen (Table I).

The lag in the excitation of vibrational energy is not observed in explosions of ozone diluted with oxygen previously reported by the authors.[14] That the absence of the effect in such explosions cannot be explained on the basis of longer explosion times is shown by comparison in Table V of explosion 2.3 (Table III) with a typical ozone explosion at nearly the same explosion temperature $T\bar{e}$. The last column gives the time elapsed between ignition and establishment of maximum pressure. It is conceivable that highly excited oxygen molecules liberated in the decomposition of ozone may readily transfer vibrational energy to molecules of their own type (oxygen molecules), whereas the transfer of such energy from freshly formed water molecules to oxygen molecules is more difficult. If the above argument is correct, barring unforeseen complications in experimental manipulation, one might also expect disappearance of the excitation lag effect in nitrogen by exploding mixtures of N_2O and H_2 diluted with N_2. Such explosions have not yet been reported.

An explanation of the water-vapor effect was proposed by Wohl and von Elbe, who suggested that OH radicals formed in the flame front

[13] Kneser, Ann. d. Physik **11**, 761, 777 (1931); **16**, 377 (1933); Phys. Zeits. **32**, 179 (1931); Zeits. f. Physik **77**, 649 (1932); Nature **129**, 797 (1932); J. Acous. Soc. Am. **5**, 122 (1933). Zener, Phys. Rev. **38**, 277 (1931); Henry, Nature **129**, 200 (1932); Eucken, Mücke and Becker, Naturwiss. **20**, 85 (1932); Sharratt and Griffiths, Proc. Roy. Soc. **A147**, 292 (1934).

[14] Lewis and von Elbe, J. Am. Chem. Soc. **55**, 511 (1933).

TABLE V. *Comparison of explosion times of ozone and hydrogen-oxygen explosions.*

Explosion	Explosion No.	$T\bar{e}$ (°K)	Time (sec.)
Ozone	3.3	2122	0.0146
H_2-O_2	2.3	2176	.0128

during the combustion of hydrogen and oxygen radiate energy by luminescence; that the radiation may be quenched by small amounts of water vapor initially present in the explosive mixture but not by the newly-formed highly energized water molecules nor by hydrogen.[15] The question concerning the efficiency of quenching the luminescence by other gases, such as O_2 and N_2, cannot be answered from the present data. The results of the dry explosions of Lewis and von Elbe in Table IV merely suggest a superposition of the excitation lag effect on the water-vapor effect. The latter predominates in explosion 1.5 because the nitrogen content represents only about 3/7 of the total inert gas. The former predominates in explosion 1.3 because nitrogen represents practically all the inert gas; in addition, the explosion time is very short, thus contributing to the excitation lag. The difference between explosions 2.6 and 1.2 is due to the fact that the excitation lag in O_2 is greater than in N_2, the former more effectively masking the water-vapor effect.

The experimental results of explosions 1.5, 1.3 and 1.2 (corresponding to 59.96 percent, 31.99 percent, 19.99 percent H_2 in air, respectively) have been verified by duplicate explosions in a larger vessel.[4]

DETERMINATION OF THE ENERGY OF DISSOCIATION $2OH+H_2 \rightleftarrows 2H_2O$

If any thermochemical data are to be derived from explosions of this kind they must obviously be free from the anomalies observed in explosions in Tables II, III and IV. The first group of explosions in Table I meets these requirements. If the slight excess of hydrogen is replaced by a slight excess of oxygen the dissociation of H_2O into OH and H_2 becomes of such magnitude as to render such explosions suitable for the determination of the energy of dissociation.

This value was determined by Bonhoeffer and Reichardt[16] with a large limit of uncertainty, namely, 128,000±5000 calories per 2 moles of H_2O, by measuring the intensity of light absorption in heated water vapor. Suitable explosions were carried out by Wohl and Magat, but the results of their three published experiments differ markedly. Nevertheless they estimate the value to be 124,000 calories.

We have made six explosions using helium instead of argon as the inert gas. Previous comparative experiments[4] in the same vessel employing identical explosive mixtures of hydrogen and oxygen and either helium or argon or various mixtures of the two inert gases gave identical maximum pressures. Considering the difference in heat conductivity of the mixtures, this agreement indicates the absence of any noticeable heat loss through the ignition rod. (The latter was of very small diameter and was made of highly non-conductive material.)

The method of calculating the energy of dissociation is that given in Case 3 above, except that instead of solving for Pe one solves for $(\Delta E^\circ_0)_{II}$, which determines the value of K_{pII}. The results are given in Table VI.

From this new value the following heats of reaction are obtained. The limits of error lie practically entirely in the above determination, since the values of the O_2 dissociation (117,300 cal.), of the H_2 dissociation (102,800 cal.), and of the heat of combustion of H_2 to H_2O (57,111 cal.) are known accurately.

$$H_2O = H + OH - (114{,}400 \pm 1000) \text{ calories}$$
$$OH = H + O - (104{,}160 \pm 1000) \text{ calories.}$$

Thus it is evident that the separation of the first H from H_2O requires more energy than the separation of the second H.

GAS VIBRATIONS IN EXPLOSIONS WITH EXCESS OXYGEN AND NITROGEN

An interesting effect observed in explosions containing excess O_2 or N_2 but never excess H_2 or A, which we believe is connected with the

[15] Concerning criticism of Garner and Tawada's (Trans. Faraday Soc. **26**, 36 (1930)) objection to this explanation see Wohl and Magat, reference 7.

[16] Bonhoeffer and Reichardt, Zeits. f. physik. Chemie **A139**, 75 (1928).

TABLE VI. *Energy of dissociation* $2OH+H_2 \rightleftharpoons 2H_2O$.

Expt. No.	m_{H_2O}	m_{O_2}	m_{N_2}	m_{He}	Pi mm Hg	Ti °K	$P_{e_{obs.}}$ mm Hg	Pe mm Hg	T_e °K	ΣmD	$\Delta E°_0$ cal.
4.4	0.286	0.078	0.028	3.512	698.8	305.9	5378	5415	2585	2.84	124500
4.7	.233	.100	.021	3.215	690.8	303.8	5468	5506	2650	3.26	124300
4.3	.251	.076	.019	2.970	698.0	305.0	5578	5617	2696	3.50	125550
4.2	.231	.105	.013	2.614	687.6	304.8	5625	5665	2773	3.74	128200
4.5	.135	.094	.007	2.694	678.4	302.8	5668	5710	2809	4.10	126750
4.6	.183	.032	.012	2.433	707.1	304.2	5913	5958	2834	4.58	126600
										Average	126000±2000

excitation lag, is that when slow-burning mixtures within certain composition limits are exploded, intense audible vibrations, which are clearly recorded on the pressure diagram, are set up.[17] These vibrations commence long before maximum pressure[18] and continue for some time thereafter. The limiting percentage of hydrogen at which the vibrations disappear was found to be about the same in a 12-inch as in an 18-inch vessel (the amplitude of the vibrations is somewhat larger in the larger sphere) and the same whether N_2 or O_2 was used as the inert gas. The vibrations are more intense in O_2 than in N_2 explosions.

The vibrations have nothing to do with the violence of the explosion, because they do not appear in richer mixtures which burn more rapidly and with greater intensity. The effect is shown in the pressure records in Fig. 1.

Moreover the effect is not due to a resonance phenomenon of the vessel because its appearance is independent of the size and shape of the vessel. Thus Campbell, Littler and Whitworth[19] observed similar vibrations in hydrogen explosions with excess oxygen in a cylinder in the same composition range as in the present experiments in a spherical vessel. Like effects were found in explosions of CH_4 or C_2H_4 with excess oxygen. Morgan[20] reported similar vibrations with certain mixtures of coal gas or CH_4 and air exploded in a cylinder. Maxwell and Wheeler[21] obtained audible vibrations with pentane and air and to a smaller degree benzene and air in a cylinder, a cube, and a sphere. In all vessels the maximum effect appeared with a mixture containing 3.5 percent pentane.

Nor are the vibrations due to a natural frequency of the diaphragm, because the same effect is found with different types of diaphragms, corrugated and plain; the frequencies of the vibrations vary decidedly with the composition of the explosive mixture, and do not correspond to the natural frequency of the diaphragm.

It is worthy of note that the vibrations are peculiarly connected with the presence of oxygen and nitrogen in the exploded gas, both of which show the excitation lag, and that the vibrations are more intense in the presence of oxygen, which has the larger excitation-lag effect.

The origin of the vibrations may be proposed as follows:

When an elementary fraction of gas burns, the O_2 and N_2 molecules do not take up their normal heat capacities immediately. The rate at which they acquire normal heat capacities depends upon time and principally temperature (probably exponential with temperature). If the combustion temperature approaches some higher critical value, the amount of gas which accumulates in the subnormal heat capacity state is small; that is, the normal heat capacity is established very soon after the passage of the flame front through an elementary fraction. The reverse is true if the combustion temperature is low, because the rate of attainment of normal heat capacity is slow. Under the latter conditions the burned gas is overexpanded. If this gas is now subjected to rather sudden adiabatic compression its temperature will rise and correspondingly its rate of attainment of normal heat capacity, as a consequence of which the mass of gas suffers

[17] Also unpublished observations by G. von Elbe and Wohl and Magat, reference 7.

[18] This is in agreement with the finding of Wawrzinick (Automobiltechnische Zeits., Feb. and March, 1933; N. A. C. A. Tech. Mem. No. 711) that the sound started before the flame reached the end of the combustion chamber, the sound being a manifestation of the pressure fluctuations inside the bomb, since both had the same frequency.

[19] Campbell, Littler and Whitworth, J. Chem. Soc. 339, 1932.

[20] Morgan, Phil. Mag. **53**, 1161 (1927).

[21] Maxwell and Wheeler, Ind. Eng. Chem. **20**, 1041 (1928).

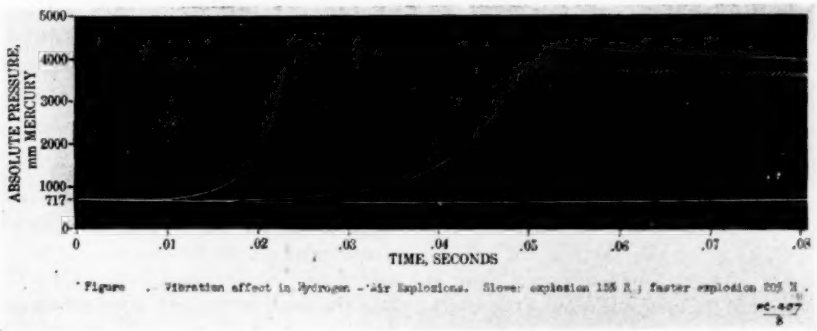

FIG. 1.

still further contraction in volume. In a spherical vessel this is to be expected (and is found) at the stage in the process where the rise in pressure is rapid, that is, where a relatively large amount of gas is burned in a short time. The mass of burned gas in the center undergoes rapid shrinkage in volume, which gives rise to a rapid mass movement of the gases inward. This may suffice to set up a pressure wave which, because of little damping, continues for some time.

In Fig. 1 the temperatures in the burned gases for any corresponding position of the flame front are about 450°C higher in the 20 percent H_2 in air mixture than in the 15 percent H_2 in air mixture. The temperatures of the gases in any layer just after the flame has passed it ranges from about 1730°C in the central layers to about 1900°C in the layers near the wall for the 20 percent H_2 mixture; correspondingly, these temperatures are 1280°C to 1450°C for the 15 percent H_2 mixture. The rate of attainment of normal heat capacity in the O_2 and N_2 molecules is much faster in the former explosion, and one may conceive that in this case subnormal heat capacity exists only in the layers of burned gas immediately behind the flame front. Thus the excitation lag which is still noticeable at the maximum pressures of such mixtures (compare Tables III and IV) is confined to the outer or last burned layers of gas while the remainder of the gas is practically fully excited. These conditions are not favorable for initiation of the gas vibrations described above. The small excitation lag effect still observable in the high-temperature explosions (compare N_2 explosions, Table III) is probably due to the very short combustion time.

RELATIONSHIP TO THE PROBLEM OF ENGINE KNOCK

That audible vibrations are concomitant with knocking in a gas engine of the Otto type, varying in intensity depending upon the severity of the knock, has been known for some time.[22] In the light of the above hypothesis on the origin of the gas vibrations described, the phenomenon of time-variable heat capacities may be given serious consideration in connection with studies of engine knock. We believe that it plays a role in many phenomena accompanying the knock, such as loss in power, increased radiation and gas vibrations. It would seem that the function of antiknock compounds is to guide the course of chemical reaction in the yet unburned charge toward preventing sudden inflammation of the latter and thus to reduce to a minimum both the setting up of a pressure impulse and the excitation-lag effect in the nitrogen gas which dilutes the charge.

[22] See for example Withrow and Rassweiler, Ind. Eng. Chem. **24**, 528 (1932); Automobile Eng. August, 1934.

Molecular Arrangement and X-Ray Diffraction in Ionic Solutions

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Solutions containing heavy ions in water were examined with Cu $K\alpha$ radiation, care being taken to avoid effects of general radiation. The diffraction patterns of saturated solutions of $Th(NO_3)_4$ and $UO_2(NO_3)_2$ consist mainly in a *pronounced* ring, *shifting* to smaller angles and getting fainter with increasing dilution. This indicates a more or less regular arrangement of the ions in the liquid, for which the name "superarrangement" will be used to distinguish it from the arrangement with smaller periodicity of the water molecules. Both arrangements are of course of the "liquid-type." The above results show that the "superarrangement" expands and gets more diffuse with increasing dilution, as might be expected. Another kind of pattern is exhibited by solutions of $AgNO_3$, $Pb(NO_3)_2$, $Ba(NO_2)_2$ and lead acetate. Here the intensity does not show pronounced maxima and minima. More especially it does *not decrease markedly* when the diffraction angle tends to zero. An explanation is offered, assuming the existence of a large fraction of undissociated molecules, with a gaseous distribution. A third class is formed by solutions of LiI, RbBr, LiBr and other alkali-halides. These yield a *broad* ring the position of which is *in*dependent of concentration. It is shown that these facts may be accounted for by ascribing this ring mainly to the interference between the scattering from a *heavy ion* and that from the *water molecules* around it. To clear up some of the above points a few experiments are made with solutions of analogous light ions. Finally a general theory on diffraction by solutions is formulated and applied to some of the experimental cases.

§1.

THERE are reasons to expect that the distribution of ions in solution is less at random than in a gas of corresponding density (or in a solution of neutral molecules). I have been occupied for some time in seeing if some information may be gained on this subject by the method of x-ray diffraction.[1, 2, 3]

From a theoretical point of view it would perhaps be preferable to investigate *dilute* solutions. The Debye-Hückel theory may then be expected to be at least a close approximation to the facts. Now this theory gives a more or less definite picture of the arrangement of the ions. The influence of this arrangement on the diffraction pattern may be easily calculated.[1] The experimental verification would, however, require very accurate (preferably absolute) measurements as the relatively strong scattering from the *solvent* is superposed on the effect in question.

For this and other reasons I have paid more attention to *strong* solutions (1–10 normal) of *heavy* ions.[4] Though at first the experimental results appeared rather puzzling, I believe that I have secured a sufficient agreement with theory to be able to draw some essential conclusions. For different reasons the interpretation is more difficult than with simple liquids: (1) the scattering from the solvent is always more or less present, (2) a large number of *a priori* possibilities exists for the "structure of strong solutions," and (3) only a very restricted number of heavy electrolytes possess a sufficient solubility to make their study possible. Because of these complications it has proved to be practically impossible to work back from the diffraction pattern to the structure in the same way as for simple liquids[5] (see, however, §8).

§2.

To get a first orientation about the problem we shall for the moment suppose that only one kind of the ions in solution scatters appreciably

[1] Prins, Zeits. f. Physik **56**, 617 (1929).
[2] Prins. Zeits f. Physik **71**, 445 (1931).
[3] Prins, Naturwiss. **19**, 435 (1931) (in particular work of Krishnamurti quoted there).
[4] See for light solutions references 1 and 3 and G. W. Stewart, J. Chem. Phys. **2**, 147 (1934).

[5] F. Zernike and J. A. Prins. Zeits. f. Physik **41**, 184, 1927 (see also work of other authors quoted there). The method indicated in this paper and developed more fully in (1) is the same as that applied afterwards by Debye and Menke to the same problems (Phys. Zeits. **31**, 797 (1930) and elsewhere). It should be observed, however, that in a more primitive form analogous ideas occur in older papers of different authors; in the first place Keesom, Debye and Raman (reference 7). I avoid the word "cybotaxis," though it aims at the same conception, because it is often used in a sense, with which I cannot entirely agree. For instance the assumption of cybotactical "groups" with "optimum size" and "expanding anisotropically" (Phys. Rev. **37**, 9 (1931)) appears to me not be to justified by the subject. With this I do not mean to detract from the main idea underlying the word cybotaxis and the many important experimental contributions connected with it.

stronger than the water molecules and that there is no large difference between the size of this ion and that of the water molecules (e.g., CsOH or LiI). In this case it appears profitable to separate the scattering power of the ion into a part equal to that of water, say A, and a "surplus scattering power" B. It is clear that the scattering power A is in this case distributed over the whole volume in much the same way as if it were filled with water alone. The amplitude which the scattering from this distribution causes at a definite point of the diffraction pattern (at a certain moment) will be called **A**, that from the rest **B**. The observed intensity is then proportional to the mean value of the square of the amplitude:

$$I=\overline{(\mathbf{A}+\mathbf{B})^2}=\overline{\mathbf{A}^2}+2\overline{\mathbf{AB}}+\overline{\mathbf{B}^2}. \qquad (1)$$

The first term in the right-hand sum simply represents the diffraction pattern of water (modified in the sense of Fig. 6). The second term may be considered as due to the interference of the scattering from the heavy ion with that from the surrounding water molecules. This term is easily seen to be of more importance than the last term if B is small. As follows from Table II (§8) and Fig. 7 this is the case with the alkali-halides (§6). On the other hand the last term is more important when B is large. This is the case with the salts of Th, U and Pb. (§§4, 5).

The last term $\overline{\mathbf{B}^2}$, of course, represents the diffraction pattern due to the surplus scattering power alone and it is through this term that the arrangement of the heavy solute particles can be detected, this being the principal object of this investigation. Regarding this arrangement two extreme cases may be considered.

(1) The ions (or molecules) of the solute may be distributed in a random* way (as in a gas).

(2) Under the influence of the mutual forces they may tend to form a more or less regular arrangement. This arrangement will then be superposed on the "liquid-arrangement" of the solvent molecules in much the same way as the "superlattice" in some alloys is superposed on the finer-meshed "lattice" constituted by the packing of all the metal atoms. This suggests the name "*superarrangement*" for the *arrangement of the solute.* It will of course presumably be of the liquid-type.

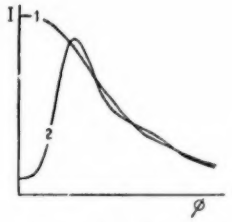

FIG. 1 Diffraction pattern of a gaseous distribution (1) and of a "liquid-arrangement" (2).

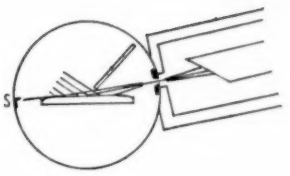

FIG. 2. Experimental arrangement for x-ray reflection at heavy liquids.

Now in the first case the diffraction pattern will be of the type represented by curve 1 in Fig. 1, while in the second case it is of type 2. Curve 1 is simply identical with the scattering curve for the isolated molecules (or ions), curve 2 is more complicated. It differs essentially from 1 in possessing a minimum at zero angle and a maximum ("amorphous ring") at some definite larger angle. Both the maximum and the minimum will be the more pronounced the more regular the arrangement is.[3] Moreover the maximum should shift to smaller angles with increasing dilution (proportionally to its cubic or perhaps square root).

It may be added that the first and second term in (1) give rise to curves of type 2, the maximum, however, *not* shifting with concentration. These notions will suffice to guide us in the description of the experiments. A more complete theory is given in §8.

§3. EXPERIMENTAL METHOD

Because of the high absorption coefficients of heavy atoms the application of the usual Debye-Scherrer method, in which the radiation passes through the substance, would require rather thin films of liquid. It is possible to make these by enclosing the liquid between mica windows[3] which are eventually drawn together by its capillary action. Some of the following results have been verified by this method. However as it is cumbersome to get the most favorable thickness (except for light liquids, Fig. 6) the

* Even in a gas the distribution is not *completely* at random as the molecules cannot interpenetrate. This "geometrical packing effect" is, however, of minor importance throughout this investigation, as the "dilution" is in general at least 1: 10.

arrangement[6] shown in Fig. 2 was in general preferred.

The x-rays from a copper target strike the liquid surface under a glancing angle of about 3° and the *reflected* pattern is photographed on a cylindrical film. The slit (1.5 mm long, 0.4 mm wide) is covered by 10μ Cu foil, the film by a homogeneous 12μ Ni foil. These foils serve to monochromatize the radiation. The most important factor in this respect is, however, that the tube is operated at a tension of not more than 15 kv. The exposition time is 3–10 hours. The concentration of the solution is kept roughly constant during this time. Sometimes the solution was stirred continuously so as to make sure that the surface layer was not different in constitution from the bulk of the solution. It should be observed that the radiation penetrates into the liquid over a distance of at least some microns; there are many reasons to assume that so thick a surface layer has the same structure as the liquid in bulk.

In this article the results are shown as photometer curves. The top line* always indicates the galvanometer zero point (100 percent blackening). Two scales are given, one for the "glancing angle" (i.e., half the diffraction angle) φ and one for the variable s, defined by.**

$$s=4\pi \sin \varphi/\lambda=2\pi/d, \quad \text{where} \quad 2d \sin \varphi=\lambda. \quad (2)$$

It should be observed that with the experimental arrangement used the blackening at large angles is shifted a little to smaller angles as the radiation from the first half of the liquid cannot reach the film in this case (Fig. 2). This effect has roughly been corrected for in the curves by a corresponding transformation of the scales, but the blackening at, say, $s>2$ is still considerably distorted. In order to locate a large angle maximum more accurately, in some cases the tube with attached spectrograph was set at the corresponding glancing angle.[6] No correction is then necessary. In general no high precision is claimed for the numerical results in this article.

The absorption in the liquid does not play a large role in distorting the blackening. The smaller the glancing angle of emergence, the stronger the absorption but also the larger the effective surface (see Fig. 2). Only at very small angles the relative intensity observed may be a *little* too low, not only because of the absorption, but also because the screen (S), which cuts off the direct (and totally reflected) ray, may also cut off part of the diffracted radiation.

§4. Results. Class I

We shall first discuss the results for thorium and uranyl nitrates, which for our purpose may be grouped together as class I.

As is apparent from Fig. 3, the principal peak present in the case of the saturated solution moves to smaller angles and gets less pronounced with increasing dilution. This points to the conception that the Th^{++++} ions are arranged in a liquid superarrangement embedded in the liquid arrangement of the water molecules, the interionic distances in the superarrangement increasing and at the same time getting less sharply defined with increasing dilution.

The position of the peaks may also be calculated or at least estimated theoretically from the number of Th ions per cm^3 solution. For this purpose a knowledge of the density of the solutions would, however, be needed and no sufficient data seem to exist. I have made a rough estimation by extrapolating the volume contraction for analogous ions and found a sufficient agreement with the experimental positions. This corroborates the above conception.

It should be pointed out that this conception is quite the opposite of the existence of colloidal or "subcolloidal" crystals of thorium nitrate or hydroxide dispersed in the medium. The above facts are incompatible with this alternative picture of the "structure of solutions" which seems to be held by many. The difference is of course that our superarrangement is *homogeneously* distributed throughout the solution. The same seems to me to be true for solutions in general;* for different cases the superarrangement may of course range from a pronounced "liquid" to a pronounced gaseous distribution.

[6] J. A. Prins, Physica **6**, 315 (1926). D. Coster and J. A. Prins, J. de Physique **9**, 153 (1928).

* The lower line has no special meaning.

** A factor 10^8 is systematically omitted in the s-values; in other words s is expressed in A^{-1}.

* Exception must be made for the case of a mixture of two liquids at a temperature close to that of complete intermiscibility.

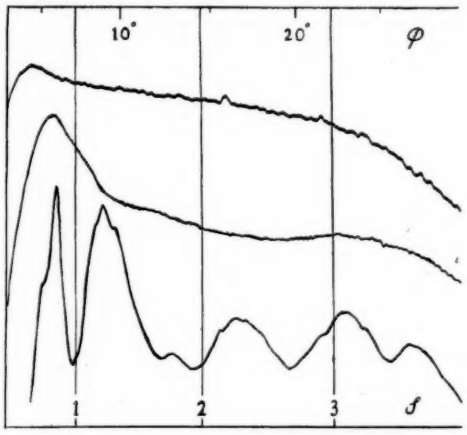

FIG. 3. Photometer curves of class I. Diffraction by thorium-nitrate solutions. Lower curve, Th $(No_3)_4 : 6H_2O$, solid, taken with broad slit. Middle curve, $Th(NO_3)_4 : H_2O = 1 : 15$, saturated solution. Upper curve, $Th(NO_3)_4 : H_2O = 1 : 40$, diluted solution.

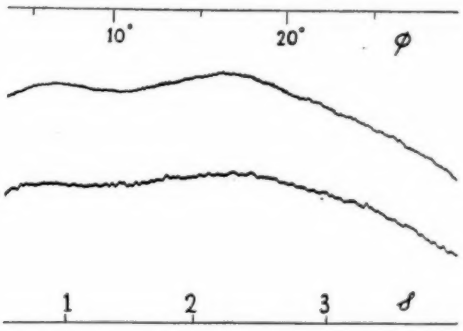

FIG. 4. Diffraction by solutions of class II. Upper curve, $AgNO_3 : H_2O = 1 : 10$. Lower curve, $Pb(NO_3)_2 : H_2O = 1 : 30$.

These considerations do not exclude the possibility that a *small* fraction of the Th ions may be present as colloidal crystals, e.g., of $Th(OH)_4$ and that these may cause the solution to show the Tyndall phenomenon.

Analogous results as with $Th(NO_3)_4$ were found in a slightly less pronounced way with $UO_2(NO_3)_2$. In this case the saturated solution is not so viscous as in the previous case and the presence of colloidal particles is still less probable.

§5. CLASS II

A more diffuse kind of diffraction pattern is shown by saturated and diluted solutions of $Pb(NO_3)_2$, Pb acetate, $AgNO_3$ and $Ba(NO_2)_2$. In this case *no sharp* maxima are present and *no marked decrease of intensity* is to be seen when zero diffraction angle is approached. These circumstances make it difficult to investigate the influence of concentration on the position of the maxima. At any rate, however, this influence does not appear to be strong. Typical photometer curves are reproduced in Fig. 4. The slight decrease at small angles in these curves *may* be an experimental defect (see §3).

As the diffraction patterns show only weak characteristics, they do not afford a good foothold for a theoretical explanation. As is shown more fully in §9, the difference between this class and the previous one may be explained by assuming that at least a large fraction of the heavy constituents are more or less distributed at random in the present case. It is reasonable to suppose these heavy constituents to be *undissociated molecules*.

It seems quite probable *a priori* that undissociated molecules should be distributed in a more "gaseous" way than ions. I feel obliged however, to point out that in reality a phenomenon *may* be present here which is of a more general nature than the difference between charged and neutral particles. I mean a difference which may crudely be designated by distinguishing between "hygroscopic" and "non-hygroscopic" particles. It is at least remarkable that the salts of class I crystallize with water of crystallization, while those of class II crystallize without it. This way of looking at the difference in question is not opposite to the previous one. On the contrary: it appears quite natural that ions should be "hygroscopic," while in general neutral salt molecules should be less so. Viewed in this way, it might be only a matter of terminology. I think it better, however, to insist on the idea of hygroscopy (or hydrophily) because this idea may also be applied to some neutral molecules. Let us first formulate the idea in question:

"Hygroscopic" particles in general crystallize with a definite or with an indefinite amount of water, their saturated solutions are very viscous and may easily be undercooled. *These properties are linked up in the present argument with a tendency of the particles to form a superarrangement, where every particle is permanently surrounded by water molecules only.*

As examples of neutral molecules to which this idea might apply I suggest fructose ("hygroscopic") and glucose (not or at least less "hygroscopic"). This seems to me to find confirmation in the x-ray patterns of the solutions.[3] The well-known difference between "emulsoidal" and "suspensoidal" *sols* may be of exactly the same kind.

§6. Class III

The diffraction patterns of the alkali-halides I have investigated differ radically from the two preceding types. They consist in a diffuse ring at a considerable angle *not* shifting appreciably with changing concentration (the contrasts, however, diminishing a little on dilution). The diameter of the ring shows only small variations for different substances, being larger for the bromides than for the iodides (Fig. 5) and slightly larger for RbBr than for NH_4Br and LiBr.

These facts find a natural explanation if we assume the ring to be largely due to the interference of the scattering from a heavy ion (I^-, Br^-, Rb^+) with that from the surrounding water molecules. As has been pointed out in §2, we may expect this effect, due to the "mixed term" in (1), to be relatively more important here than in the previous cases, where the surplus scattering power is larger. For the same reason the absence of an "inner ring" in the present case does not prove that all tendency to a super-arrangement is absent, but only that it cannot be very strong.*

The following numerical data corroborate the above explanation. From theoretical considerations we may expect the diffraction angle of the maximum 2φ to be related to the distance a between the center of the heavy ion and that of a water molecule touching it by the relation:

$$\lambda = 2(fa) \sin \varphi.$$

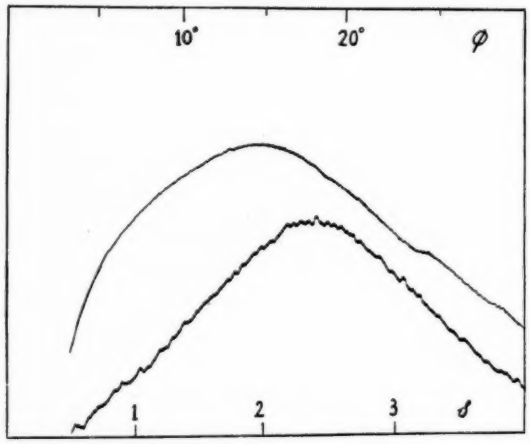

Fig. 5. Diffraction patterns, class II. Solutions of alkali-halides. Upper curve: LiI : H_2O = 1 : 15 molar. Lower curve: RbBr : H_2O = 1 : 9 molar.

Here f is a factor for which by slightly different ways of reasoning any value between 0.8 and 1 may be found.[7] We shall here somewhat arbitrarily put it equal to 0.85. The preceding formula may then be written:

$$a = \lambda/1.7 \sin \varphi$$

or by referring to (2)

$$a = 7.4/s. \qquad (3)$$

The values for a calculated by means of this formula from our experimental s-values are given in Table I (third column). They may be compared with the values calculated from the well-known ionic radii, derived from crystallographic data (water molecule r = 1.4A).

Table I. *Distances in A between centers of ions and of surrounding water molecules.*

Ion	s observed	a from (3)	a from ionic radii
I^-	2.0	3.7	3.6 = 2.2 + 1.4
Br^-	2.3	3.2	3.4 = 2.0 + 1.4
Rb^+	2.5	3.0	2.9 = 1.5 + 1.4
Th^{++++}	3.0	2.5	2.5 = 1.1 + 1.4

The numerical agreement between column 3 and 4 is better than our rough measurements and calculations give a right to expect and might even

* It is possible for example that in Fig. 5 the left-hand part of the curve for Li I is partly due to such an inner ring. Because of its diffuseness, however, it would be hardly possible to observe an eventual shift with concentration. On the other hand in class I (and perhaps in class II too) there seems also to be a large angle maximum independent of concentration. With $Th(NO_3)_4$ it is situated at about s = 3.0. It is reasonable to explain this maximum as due to the "mixed term" too. In all cases a large fraction of the intensity at $s \geqq 2$ is of course due to the term $\bar{A}^2$ in (1) i.e., to the water alone.

[7] W. H. Keesom and J. de Smedt, Proc. Amst. Acad. **25**, 118 (1922); C. V. Raman and K. R. Ramanathan, Proc. Ind. Ass. for Cultiv. Science **8** (2), 127 (1923). P. Debye, Phys. Zeits. **28**, 135 (1927). See also references 6 and 1.

be slightly fortuitous. But the parallelism between the two columns can hardly be accidental and is a strong support in favor of the interpretation of the results advocated in this paragraph.

The preceding diffraction patterns of class III have in common with those of class I that the intensity decreases markedly when the diffraction angle tends to zero. It cannot be assured experimentally that the intensity tends to zero and indeed it follows from theory (§§8, 9) that only a certain *not very small* limiting value should be approached (Fig. 8). Nevertheless the experimental decrease may be said to be clearly marked.

This feature gets more and more lost when the following series is successively investigated: (class III), $CsNO_3$, $SrBr_2$, $BaCl_2$, $Ba(NO_2)_2$, $Ba(NO_3)_2$, Ba acetate, (class II). This suggests that the salts between classes III and II must be considered as transition cases from class III to class II, in good accord with their position in the periodic system.

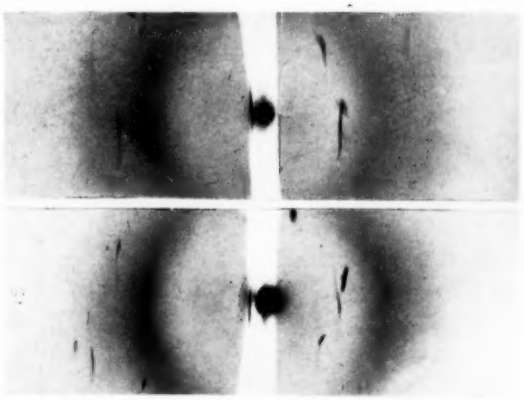

FIG. 6. Debye-Scherrer photographs taken with Cu $K\alpha$ radiation penetrating a liquid layer 0.5 mm thick between mica windows 3μ thick. Upper figure, pure water. Just outside the main ring a weaker second ring is present. Lower figure, LiOH : $H_2O = 1 : 10$ (saturated). The two rings have fused to one of slightly larger diameter than the main ring of pure water.

§7. Light Ions and Water

To make sure that the small angle intensity observed with $Pb(NO_3)_2$ etc. (§5) is not due to the presence of the NO_3^- ion alone I have also photographed the diffraction pattern of a $NaNO_3$ solution with a mole ratio of 1 : 10. No small angle scattering of any importance was observed. The pattern resembled that of an equivalent NaCl solution. This pattern may be interpreted as mainly due to the arrangement which the *water molecules* assume in the electric field of the ions, these being too light to contribute appreciably to the diffraction pattern themselves.

This conception of a *rearrangement of water by ions* is due to Bernal and Fowler[8] who made use of experimental results of Meyer.[9] According to this conception in pure water the H_2O molecules are arranged in a "tetrahedral" and more especially in a "quartz-like" liquid arrangement. This arrangement is due to the peculiar electrical constitution of the H_2O molecules consisting of two positive and two negative poles arranged tetrahedrally in the (almost spherical) surface of the molecule. This constitution causes every molecule to be surrounded by only *four* neighboring molecules which join it each with one of their poles (+ to − of course). This tetrahedrical arrangement is, however, wrenched loose by the strong electric field of the ions, if these are introduced. A more or less close packing, where every molecule has more than four neighbors, is the result. This not only accounts for the well-known volume contraction observed on adding an electrolyte to water but also for the changing of the peculiar x-ray diffraction pattern of water to the more universal pattern of a close-packed liquid (see Fig. 6).

Fig. 6 represents some experiments I have made with solutions of NaOH and LiOH to confirm and extend the analogous results of Meyer, who used NaCl and LiCl solutions. To these the objection might be raised that the *scattering* by the Cl^- ion contributed appreciably to the modified pattern. This objection may be shown not to be very serious, as has already been observed by Meyer, but I have thought it would be more convincing to show the effect with LiOH. In this case the objection loses all significance as the scattering by the Li^+ ion is negligible and that of the OH^- ion may well be identified with that of a H_2O molecule.

Incidentally it may be mentioned that I have the impression that 5 normal solutions of LiOH and NaOH do not produce *quite* so large a modi-

[8] J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933).
[9] H. H. Meyer, Ann. d. Physik **5**, 701 (1930).

fication of the pattern as equivalent solutions of LiCl and NaCl.

§8. Theory

Without an exact theoretical treatment any discussion would become too vague. We shall make use of the theory given by Zernike and Prins[5] for ordinary liquids, as it is very well suited for the present case of solutions. In this theory the arrangement of the molecules and ions is expressed by a *distribution law* $g(r)$ for the *distances* between the molecular (or ionic) centra. As was shown by the authors it is then possible to calculate the x-ray pattern from the distribution function and *vice versa*.[5]

For the sake of simplicity we shall begin by supposing the water to contain only one kind of heavy ions, or stated more accurately: We suppose a certain volume to contain N particles of scattering power (see below) A and n particles of scattering power a; the particles of the first kind will be called (water) molecules, those of the second kind ions. The scattering by the volume in question will then at some definite point of the diffraction pattern give rise to an amplitude:

$$A_1+A_2+\cdots+A_N+a_1+a_2+\cdots+a_n,$$

where the separate terms indicate the amplitudes of the elementary waves from the different particles. Now what is wanted is the intensity, in other words the mean square of the above quantity:

$$I=\overline{(A_1+A_2+\cdots A_N+a_1+a_2+\cdots a_n)^2}.$$

This works out to a sum of all possible products, occurring in three types:

$$\sum_{NN}A_kA_l+2\sum_{Nn}A_ka_l+\sum_{nn}a_ka_l.$$

The mean value, e.g., of the first sum may now be found by first taking together all terms having A_k as first factor, then taking the mean of this aggregate keeping A_k constant and finally taking the mean over A_k. This gives

$$\overline{A_k(A_1+A_2+\cdots+A_k+\cdots+A_N)}$$
$$=\overline{A^2}+\bar{A}^2\int_0^\infty dr4\pi r^2g(r)[\sin(sr)/sr].$$

Here A denotes the mean* amplitude of the elementary wave scattered by one molecule. For spherically symmetrical molecules $\overline{A^2}=\bar{A}^2$ and so we may designate both quantities with A^2. This then is the exact definition of the "scattering power" A introduced above. As regards the integral in the right-hand expression it is equivalent to the mean sum over l (excluding $l=k$) figuring in the left-hand expression. The sin $(sr)/sr$ and the distribution function $g(r)$ enter into it in virtue of the phase differences existing between A_k and A_l for all possible distances and diffraction angles. Finally the second summation (over k) now yields a factor N (or n in the third sum) as all indices have disappeared. So finally:

$$I=NA^2\left[1+\int_0^\infty dr4\pi r^2g(r)\frac{\sin(sr)}{sr}\right]$$
$$+2NAa\int_0^\infty dr4\pi r^2g'(r)\frac{\sin(sr)}{sr}$$
$$+na^2\left[1+\int_0^\infty dr4\pi r^2g''(r)\frac{\sin(sr)}{sr}\right] \quad (4)$$

or, designating the three integrals, respectively, by $G(s)$, $G'(s)$, $G''(s)$:

$$I=NA^2[1+G(s)]+2NAaG'(s)$$
$$+na^2[1+G''(s)]. \quad (5)$$

In these formulae primed letters refer to the distribution of ions with respect to a water molecule; doubly primed letters refer to the distribution of ions with respect to one of them.

If the case of a 1 : 10 Li I solution is considered as an example and the presence of the Li^+ ions is disregarded, then one may put $n=N/10$, $a=5$A (see Table II). This renders the second term more important than the third, which explains the remarkable features of the diffraction patterns of class II, mentioned in §4. On the other hand with higher values of a the last term gets more important. *If* the distribution function g'' corresponds to a superarrangement this last term may be held responsible for the shifting peak found with class I (§4). *If* on the other hand the distribution expressed by g'' is more or less a gaseous one, the presence of the

* In (4) A means the maximal amplitude. This causes $\frac{1}{2}NA^2$ to appear where here in (5) NA^2 appears.

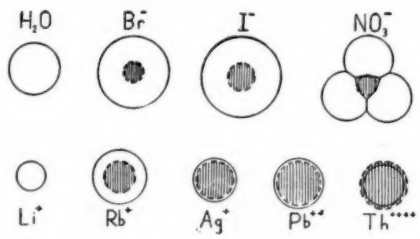

FIG. 7. Dimensions and scattering power of some ions. If the shaded volume is supposed to contain an electron density 10 times that of water it will give the right surplus scattering power.

last term accounts largely for the features of class III, at least in the case of lead salts. In the case of $AgNO_3$ the preponderance of the third term is dubious and a closer examination (§9) is needed to check the agreement between theory and experiment.

In all cases our principal aim is to get a knowledge about g''. This may be derived from an accurate determination of $1+G''$. This object may be facilitated by *comparing* the diffraction pattern for a heavy electrolyte such as CsOH with the one for an analogous light electrolyte such as NaOH. If the two diffraction patterns, reduced to the same value of N, are subtracted, we should expect the first term to disappear, while the second term might perhaps be estimated with sufficient accuracy to find the last term. This method was alluded to in the last part of §1.

In Fig. 7 and in Table II numerical data on the

TABLE II. *Dimensions and scattering power of some ions and of H_2O.*

	H_2O	Br^-	I^-	NO_3^-	Rb^+	Ag^+	Pb^{++}	Th^{++++}
Radius in A	1.40	1.95	2.20	1.3–2.6	1.49	1.13	1.32	1.10
Effective number of electrons	10	35	53	32	35	45	74	80
Surplus number of electrons	0	7(15)	14(25)	2(11)	23	40	66	75
Radius broken circle Fig. 7	0	0.58	0.73	0.5	0.85	1.03	1.22	1.27

scattering powers and dimensions of the ions, discussed in this article, are exhibited. The scattering power is represented by the "effective number of electrons" which may be found from the total number of electrons by eventually taking into account the anomalous scattering of K and L electrons. For some purposes it is more useful to know the "surplus scattering power," obtained by diminishing the previous quantity by the amount of electrons that would be needed to fill the volume of the ion with the same electron density as is present in a water molecule.* It is easy to transcribe formulae (4) and (5) under the assumption that a denotes the *surplus* scattering power and N the *total* number of particles. The first term should then almost completely coincide with the *lower* diffraction pattern exhibited in Fig. 6.

§9. ONE-DIMENSIONAL MODELS

We shall assume in this paragraph that no forces exist between any particles in the liquid except of course insofar as they keep it together in a definite volume. It is then possible in principle to calculate the diffraction patterns from (4), as the g-functions are completely defined by this assumption and by the dimensions of the particles and the available free space. In practice it is, however, too difficult to perform this calculation in the three-dimensional case. The analogous calculation is, however, easily made rigorously in the one-dimensional case and the result may be expected to provide a rather good picture of the corresponding three-dimensional case. We shall show in this way that the diffraction patterns of class II and III may be understood without introducing new principles.

Consider a straight line of length L containing a large number αN of "molecules" of length a and scattering power A and a large number $\beta N(\alpha+\beta=1)$ of "ions" of length b and scattering power B. The total free space $L-\alpha Na-\beta Nb$ divided by N will be called the mean free space per particle l. On the assumptions stated above the arrangement is a matter of geometrical probability. By an argument analogous[10] to that used by Zernike and Prins[5] the following expression may be derived for the diffraction pattern of the arrangement (considered as section of a plane "grating" at normal incidence):

$$I/N = \text{real part of } \alpha A^2+\beta B^2 + \frac{2(\alpha A e^{isa/2}+\beta B e^{isb/2})^2}{1-ils-(\alpha e^{isa}+\beta e^{isb})}. \quad (6)$$

* Instead of this density the electron density of close-packed water *in bulk* should be taken if the ion is relatively large. The corresponding figures have been added in parentheses in Table II. The truth lies somewhere between these numbers and those preceding them.

[10] The mathematical treatment may be simplified by introducing generating functions for the intermolecular distances.

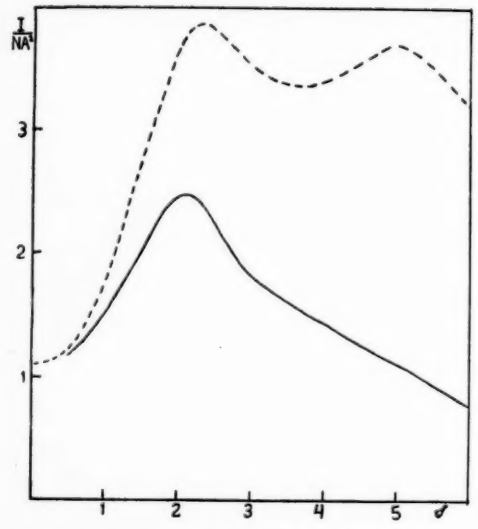

FIG. 8. Theoretical diffraction pattern for one-dimensional I^- solution (1 : 10). Broken curve represents expression (6). Full curve is derived from it by taking into account the "atomic scattering powers" for H_2O and I^- from the Thomas-Fermi model.

In this expression $s=2\pi \sin \psi/\lambda$ (ψ=diffraction angle), this quantity is the analog of the variable s from (1) in the three-dimensional case.

To get the case of a 1 : 10 I^- solution we put: $\alpha=0.9$, $\beta=0.1$, $b=2a$, $l=a$, $B=5A$, $a+l=2.8$A. The result is shown in Fig. 8, which should be compared* with Fig. 5.

To discuss expression (6) we may separate it in four terms: (1) The term $\alpha A^2+\beta B^2$ which will be called the "gas-term." It is the most important term for large values of s. (2) The first term arising from working out the quadratic numerator contains the factor A^2 and will be called the "water-term." (3) The second term arising in the same way and containing AB will be called the "mixed term." (4) The third term arising in the same way and containing B^2 will be called the "ionic term."

In our case the mixed term is slightly more prominent than the water term and both terms are more prominent than the ionic term. If the mixed term alone were present the position of the maximum would roughly correspond to a "grating constant" $a+l+b+l$ in other words to the mean distance between the centers of an ion and a neighboring water molecule. With increasing dilution the water term gets more predominating and the maximum slowly shifts to the position corresponding to the distance between adjoining water molecules. This shift is, however, so slow that it is no wonder that it has not been noted experimentally (§6) with concentrations varying at most from 1 : 5 to 1 : 20. With the other alkali-halides the difference between the dimensions of the ion and the water molecule is too small to give rise to an appreciable shift.

The same model may more or less serve for the $AgNO_3$ and $Pb(NO_3)_2$ solutions when the salt *molecule* is substituted for the I ion. It has in both cases roughly the same dimensions as the I ion. The principal difference consists in the following two points:

I. The scattering power of the salt molecule is larger than that of the I ion.

II. The "molecular scattering curve" for the salt molecule shows a steeper decrease beginning at a smaller angle than the "ionic scattering curve" of I^-.

Circumstance I renders the gas term 1 (see above) relatively more prominent. This makes the minimum at small angles less marked. Circumstance II has an analogous effect. A rough calculation shows that even with $AgNO_3$ (and *a fortiori* with Pb salts) the practical disappearance of the minimum found experimentally (Fig. 4) may be well explained in this way.

The shifting peak of class I can of course *not* be explained by the model of this paragraph. It is due to special forces (§5) causing a superarrangement. On the other hand we may now be pretty sure that an analogous superarrangement is not present to an appreciable degree with class II (and that with class III it cannot be very strong) as the experimental results appear to be explained without introducing it.

At this stage I believe that only very accurate (and if possible absolute) measurements could provide more precise information. It is certainly disappointing that the elements 85 and 87 are not available for this purpose.

* For different reasons the s-scales cannot be expected to correspond exactly. A satisfactory agreement may, however, be established in this respect, too, by a more careful elaboration of the correspondence.

The Energies of Hydrocarbon Molecules[1]

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(Received November 24, 1934)

The energies of a number of hydrocarbon molecules have been calculated by the Heitler-London-Pauling-Slater method with two objects in view, first, to see if this simple theory leads to the correct energies of formation, and second, to determine what significance can be attached to the empirical additivity rule for bond energies. Our equations involve three parameters, which roughly speaking, determine the gross energies of a C−H bond, a C−C bond, and a C=C bond. These have been evaluated from the observed energies of methane, ethane and ethylene. The energies calculated for other hydrocarbons then agree surprisingly well with the observed values. Nevertheless, the validity of an empirical bond additivity rule seems to be purely fortuitous. The calculations further indicate that the theoretical significance ordinarily ascribed to the so-called "observed resonance energies" is a very questionable one.

VAN VLECK,[2,3,4,5] Penney[6,7,8] and their collaborators have applied the Heitler-London-Pauling-Slater theory with considerable success in explaining the structure of polyatomic molecules. While the theory has thus shown its adequacy for such semiqualitative considerations, it would indeed be optimistic to expect of it an equally good account of the total energies, that is, the energies liberated in forming molecules from widely separated atoms in their normal states. Our calculation of the total energies of a number of hydrocarbon molecules thus affords a much more severe test of the approximations involved in the H-L-P-S procedure. The calculation is additionally interesting since through it one may hope to obtain a theoretical explanation of the empirical bond additivity rule.

Let us suppose that a hydrogen orbit, α, is paired to a carbon orbit, a. The total interaction energy between the hydrogen and carbon atoms is then

$$W_{HC}=3/2J_{a\alpha}+S_{HC}, \qquad (1)$$

where $S_{HC}=Q_{HC}-1/2\sum_{i=s,\sigma,\pi,\pi'}J_{ai}$.

Here the J's are the ordinary exchange integrals, and Q_{HC} is the Coulomb energy. The steric term, S_{HC}, is a function only of the internuclear distance and is quite independent of the choice of carbon orbits,[9] i.e., of the angles between the bonds. Advantage has been taken of this invariance to write S_{HC} in terms of unhybridized orbits. The individual J's, on the other hand, do depend on the bond angles. If the hydrogen orbit is not paired to any orbit on the carbon atom the first term in (1) drops out and only the steric term is left. In a similar way, the interaction between two carbon atoms is

$$W_{CC'}=3/2\sum_{\text{pairs}}J_{ii'}+S_{CC'}, \qquad (2)$$

where $S_{CC'}=Q_{CC'}-1/2\sum_{i,j=s,\sigma,\pi,\pi'}J_{ij}$.

To the approximation of pure electron pair bonding, the total energy of the molecule is

$$W=\sum_{ij}W_{H_iC_j}+\sum_{i<j}W_{C_iC_j}+\sum_i W_v(C_i)+\sum_{i<j}M(H_iH_j). \qquad (3)$$

The last sum in (3) represents the hydrogen-hydrogen repulsions. $W_v(C_i)$ is the energy of the valence state of the ith carbon atom, the normal state of the carbon atom being taken as the zero of energy. Because of the influence of the $L-S$ structure of the carbon atom $W_v(C_i)$ is not necessarily the same for all carbon atoms in the molecule, but depends on the angles

[1] A preliminary account was given at the Ann Arbor Meeting of the American Physical Society, June, 1934. (Phys. Rev. **46**, 335A (1934)).

* National Research Fellow.

[2] J. H. Van Vleck, J. Chem. Phys. **1**, 177 (1933).

[3] J. H. Van Vleck, J. Chem. Phys. **1**, 219 (1933).

[4] J. H. Van Vleck, J. Chem. Phys. **2**, 20 (1934).

[5] J. H. Van Vleck, J. Chem. Phys. **2**, 297 (1934).

[6] W. G. Penney, Proc. Roy. Soc. **A144**, 166 (1934).

[7] W. G. Penney, Proc. Roy. Soc. **A146**, 223 (1934).

[8] W. G. Penney, Proc. Phys. Soc. (London) **46**, 333 (1934).

[9] This is a simple consequence of the unitary character of the transformation from one set of orbits to another. A proof is given by Penney, reference 7.

between the bonds made by the atom in question. In the cases we will consider, $W_v(C_i)$ lies between 7 v and 7.5 v. For any particular molecular model, the third and fourth sums of (3) can readily be evaluated by means of formulas given by Van Vleck.[10] The first and second sums of (3) contain terms of two types: interactions between adjacent atoms, i.e., between atoms which are bonded to each other, and steric interactions between distant, unbonded atoms. It will be seen from (1) and (2) that the steric terms consist of sums of terms of opposite sign which largely annul each other. The steric terms, W_{HC} and $W_{CC'}$, between distant atoms are certainly small, and we shall provisionally suppose that they are so small that they may be neglected. If we obtain good agreement between the calculated and observed energies, we can regard this supposition as substantiated. The terms W_{HC} between adjacent atoms can be calculated by using Van Vleck's[4] values of the exchange integrals $N_{\sigma\sigma}$, N_{ss}, $N_{\sigma s}$, and by determining S_{HC} from the observed energy of methane. We shall neglect the small differences in internuclear distances in different molecules. The $W_{CC'}$ terms between adjacent carbon atoms appear at first glance much more troublesome, since they involve numerous exchange integrals, $C_{\alpha\beta\gamma\delta}$ in Penney's notation,[6] whose values are not reliably known. The problem is greatly simplified, however, by the following considerations, which we shall illustrate by reference to Penney's model of the ethylene molecule.[6] In this model W_{HC} is the same for all four hydrogen atoms, and is a function of the angle ω (see insert in Fig. 1. Of course for ethylene the lower C atom is also bonded to two H atoms in the same manner as the upper one). $W_{CC'}$ can be written

$$W_{CC'}=W_{C-C'}+3/2\alpha, \qquad (4)$$

where α is the exchange integral $J_{\pi\pi}$ in the notation of (2), or $-C_{\pi\pi\pi\pi}$ in Penney's notation. The first term in (4) is the bonding energy of the principal carbon-carbon bond (the one directed along the C−C line), the second term represents the energy of the second carbon bond (the $\pi-\pi$ bond), which is independent of ω and

[10] Reference 4. Note corrections given in reference 5.

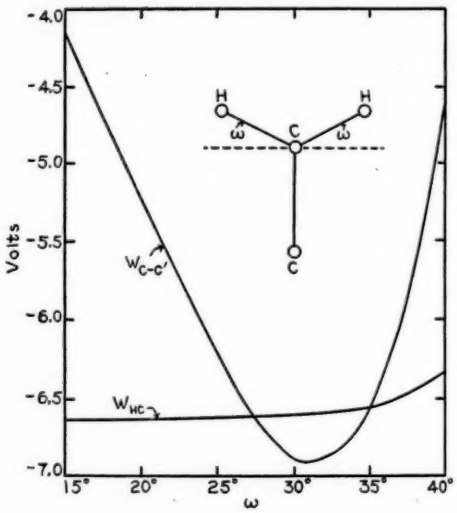

FIG. 1. In computing $W_{C-C'}$ it has been supposed that the hybridization ratios of the two orbits in the C−C bond are equal, an obvious condition in order that $W_{C-C'}$ be a minimum.

of no interest for our present purposes. In Fig. 1 we have plotted W_{HC} as a function of ω. It will be seen that the curve is very flat over a wide range of values of ω. Hence if we suppose that $W_{C-C'}$ has a sharp minimum in this range, the carbon-hydrogen interaction plays very little part in determining the form of the molecule: the hydrogen bonds simply arrange themselves in directions which bring the carbon single bond energy to its minimum. The stability of the benzene ring immediately suggests that the minimum of $W_{C-C'}$ should fall at $\omega=30°$; we shall assume this to be so in our further calculations. One may test this assumption by using the values of the various exchange integrals, $C_{\alpha\beta\gamma\delta}$, suggested by Penney.[11] The variation of $W_{C-C'}$ with ω found in this way is shown in Fig. 1. We see that with this choice of exchange integrals, $W_{C-C'}$ does indeed have a sharp minimum at 30°.

For Van Vleck's θ type bonds[12] the curves obtained for W_{HC} and $W_{C-C'}$ are again very

[11] Reference 7. The set of values labeled (2) has been employed since Dr. Penney informs the writer that these are probably the best estimate.

[12] See Fig. 2 and Eq. (33), reference 3. In this case the C atom is bonded to three H atoms and another C atom. If the C−C line is taken as the polar direction, the azimuths of the three H atoms are 0°, 120°, 240°, respectively, rather than 0°, 180°, as shown in Fig. 1, and θ is the angle CCH.

similar in appearance to those shown in Fig. 1. It thus appears that for all molecular models involving bonds of the ω and θ types, maximum stability is attained when the various bonding angles are such that $W_{C-C'}$, for each carbon-carbon bond, takes on its minimum value.[13] In order to find the energy of the principal carbon-carbon bond we accordingly need not know the values of the individual carbon-carbon exchange integrals, $C_{\alpha\beta\gamma\delta}$ but only that of the particular linear combination of them involved in $W_{C-C'}$ at its minimum. Hereafter, $W_{C-C'}$ is to be understood as representing the minimum value of this quantity, unless otherwise stated. We shall determine $W_{C-C'}$ from the observed energy of ethane. The only other carbon-carbon exchange integral which plays an important role in our calculations is α, which, as (4) shows, fixes the energy of the second bond in a carbon-carbon double bond. α will be evaluated from the observed difference between the energies of ethane and ethylene.

Before we proceed to the explicit calculations, one troublesome point must be examined. The observed molecular energy is the sum of the "electronic" energy and the energy of nuclear motion. Our calculations should refer only to the electronic part of the energy. However, it is not usually possible to actually compute the nuclear energy. This can be done approximately in a few cases. Zahn[14] estimates that the nuclear energy of methane is 1.25 v, that of ethane is 1.97 v, and each additional CH_2 group increases the nuclear energy by about 0.7 v. In a similar way, using the data of Mecke[15] and of Eucken and Parts[16] and Sutherland,[17] one finds the value 1.4 v for ethylene and 0.7 v for acetylene. It will be seen that these figures can be represented fairly well by a rule of the bond additivity type which assigns a nuclear energy of about 0.3 v to each C—H bond, and an energy of about 0.1 v to each carbon-carbon bond. We must suppose that this representation of the nuclear energies is sufficiently accurate for our purposes. The nuclear energies then need not be taken into account explicitly: their only effect will be to increase the "observed" value of S_{HC} by 0.3 v, and of $S_{CC'}$ by 0.1 v.

From the observed energy of methane, $W(CH_4) = -16.3$ v, we find, by a calculation similar to that given by Van Vleck,[4] that W_{HC} for methane is -6.47 v. Once this value is determined it is a simple matter to compute W_{HC} for any other arrangement of carbon orbits.

For ethane we shall use the model proposed by Penney.[6] In order to make $W_{C-C'}$ a minimum we must take $\theta = 112°$, this being the value of θ which gives the same hybridization ratio in the C—C bond orbits as does $\omega = 30°$. The energy of ethane is then

$$W(C_2H_6) = 6W_{HC}(\theta = 112°) + W_{C-C'} + 2W_v(C) + \sum_{i<j} M(H_iH_j). \quad (5)$$

The values of the various terms are: $W_{HC}(\theta = 112°) = -6.42$ v, $W_v(C) = 7.06$ v, $\sum M(H_iH_j) = 3.72$ v. In computing $\sum M(H_iH_j)$ we have taken the carbon-hydrogen internuclear distance to be 1.08A, and the carbon-carbon distance to be 1.37A. From the observed energy, $W(C_2H_6) = -27.57$ v, we find $W_{C-C'} = -6.89$ v.

The difference in energy between ethane and ethylene is

$$W(C_2H_6) - W(C_2H_4) = 6W_{HC}(\theta = 112°) - 4W_{HC}(\omega = 30°) - 3/2\alpha + 2[W_v(C) - W_v(C')] + \sum M(H_iH_j) - [\sum M(H_iH_j)]'.$$

The primed terms here refer to ethylene. Using $W_{HC}(\omega = 30°) = -6.59$ v, $W_v(C') = 7.20$ v, $[\sum M(H_iH_j)]' = 1.09$ v, $W(C_2H_6) - W(C_2H_4) = -5.73$ v, we find $\alpha = -2.72$ v. It should be noted that this value of α is entirely compatible with Penney's calculation of the twisting frequency of ethylene,[8] since his calculation determines not α, but $\alpha - \alpha'$, where $\alpha' = -C_{\pi\pi'\pi'\pi}$ ($\alpha' = J_{\pi\pi'}$ in the notation of (2)). Pauling and Wheland[18] give $\alpha = -1.5$ v, but, as we shall see,

[13] If, with ω type bonding, the carbon atom is bonded to two other carbons and one hydrogen, rather than to two hydrogens and one carbon, the influence of the H—C interaction is considerably more important than indicated by Fig. 1. Fortunately, in this case the H—C interaction, as well as the C—C interaction, favors the 30° configuration. See reference 7.

[14] C. T. Zahn, J. Chem. Phys. **2**, 671 (1934).

[15] R. Mecke, Zeits. f. physik. Chemie **B17**, 1 (1932).

[16] Eucken and Parts, Zeits. f. physik. Chemie **B20**, 184 (1933).

[17] Quoted by Penney, reference 8.

[18] L. Pauling and G. W. Wheland, J. Chem. Phys. **1**, 362 (1933).

the argument which leads to their value is a very dubious one.

It is now a simple matter to compute the energies of hydrocarbons for which simple electron pair bonding is a reasonable approximation, i.e., which do not involve resonance effects. In our models of molecules of the ethane and ethylene series, the carbon atoms are arranged in a staggered chain. The staggering is of course necessary to preserve the 120° angles between the carbon-carbon bonds. For example, for propane, the bonding of the two end carbon atoms is of the θ type, with $\theta=112°$, while the bonding of the center carbon atom is of Van Vleck's class (a) type,[19] with $(180°-2\omega)$, the angle between the carbon-carbon bonds, equal to 120°. The energy of propane is thus[20]

$$W(C_3H_8)=6W_{HC}(\theta=112°)+2W_{HC}(\omega=39.3°)$$
$$+2W_{C-C'}+2W_v(C_1)+W_v(C_2)+\sum M(H_iH_j),$$

with

$$W_{HC}(\omega=39.3°)=-6.37v, \quad W_v(C_2)=7.10 \text{ v},$$
$$\sum M(H_iH_j)=4.90 \text{ v},$$

and the remaining terms as given in (5). This gives $W(C_3H_8)=-38.92$ v. The observed value is -38.9 v. The results of the calculations for a number of molecules are given in Table I.

The approximation of simple electron pair bonding is inadequate for molecules such as acetylene and benzene which involve multiple $\pi-\pi$ bonds. Here more accurate methods must be employed. For acetylene, we use a linear model. If the axis of figure be the z axis, each carbon atom has a π orbit directed along the x and y axes. The interaction between these four orbits must be considered as a four-electron problem, rather than as two electron pairs with a small interaction term. The energy can be written $W(C_2H_2)=W_0+W_1$, where $W_0=2W_{HC}+W_{C-C'}+2W_v(C)+M(H_1H_2)$, and W_1 is the energy due to the four π orbits. For this model $W_{HC}=-6.61$ v, $W_v(C)=7.51$ v and $M(H_1H_2)$ is negligible. Unlike the other cases we consider, for acetylene $W_{C-C'}$ does not have its minimum value. In order to estimate its deviation from the minimum we have used Penney's values of the carbon-carbon exchange integrals. The deviation is found to be 0.33 v, thus $W_{C-C'}=-6.56$ v. The familiar four-electron formula[21] gives

$$W_1=-\{2[(\alpha-\alpha')^2+(\alpha-K_{\pi\pi'})^2$$
$$+(\alpha'-K_{\pi\pi'})^2]\}^{\frac{1}{2}}+\alpha+\alpha'+K_{\pi\pi'}, \quad (6)$$

where $\alpha'=-C_{\pi\pi'\pi'\pi}=J_{\pi\pi'}$, and $K_{\pi\pi'}$ is the intra-atomic exchange integral between the π orbits. The ordinary four-electron formula comprises only the term under the radical sign in (6); the necessity of adding the remaining terms can be seen as follows. The term under the radical sign represents the complete contribution to the energy from the four π orbits, hence W_0 should contain no contribution from these orbits. However, if we examine W_0 in detail we see from (2) that $S_{CC'}$ contains, for each choice of a pair of π orbits, one on each carbon atom, either the term $-\frac{1}{2}\alpha$ or the term $-\frac{1}{2}\alpha'$, depending on the relative orientation of the orbits. The total contribution to $S_{CC'}$ of our four π orbits is thus $-\alpha-\alpha'$. Similarly, from Van Vleck's formula for $W_v(C)$, we see that the contribution of our π orbits to $W_v(C)$ is $-\frac{1}{2}K_{\pi\pi'}$. The term $\alpha+\alpha'+K_{\pi\pi'}$ must thus be added to the radical in (6) in order to correct for these steric terms which appear in W_0. A simpler example of the same point is afforded by noting from (2) or (4) that the difference in energy between a carbon single bond and a carbon double bond is $\frac{3}{2}\alpha$, not α as one might at first suppose. The energy of the $\pi-\pi$ bond is indeed α, but it must be remembered that if this bond were lacking, the interaction of the two π orbits would contribute a term $-\frac{1}{2}\alpha$ to the energy, and this no matter what the choice of carbon orbits. The difference in energy due to the presence of the $\pi-\pi$ bond is thus $\frac{3}{2}\alpha$. A similar interpretation holds for the added terms in (6).

According to Van Vleck,[5] $K_{\pi\pi'}=0.56$ v. The exchange integral α' can be obtained from the difference $\alpha-\alpha'=-0.72$ v deduced by Penney from the observed twisting frequency of ethylene. Using these values we find $W(C_2H_2)=-14.9$ v, compared to the observed value, -15.2 v. Since most of the stability is due to W_1, W_0 amounting

[19] See Fig. 1 and Eqs. (32) and (34), reference 3.

[20] The value $\omega=39.3°$ is determined from the constraint between the angles given by Eq. (32), reference 3.

[21] F. London, Zeits. f. Electrochemie **35**, 552 (1929); J. C. Slater, Phys. Rev. **38**, 1109 (1931).

to only -4.76 v, the agreement between the calculated and observed values is a very nice confirmation of the value we have found for α.

The interaction of the π orbits in benzene must be treated as a six electron problem. The energy is $W=W_0+W_1$, with

$$W_0=6W_{HC}(\omega=30°)+6W_{C-C'}+6W_v(C)+\sum M(H_iH_j),'$$

and[22]

$$W_1=2\alpha+5\gamma/2-[9(\alpha-\beta)^2+4(\alpha-\gamma)^2]^{\frac{1}{2}}. \quad (7)$$

Here β and γ are the values of $-C_{\pi\pi\pi\pi}$ at internuclear distances corresponding to the distance between alternate carbon atoms, and the distance between diagonally opposite atoms, respectively. The steric correction term $3\alpha+3\beta+3\gamma/2$ is included in W_1. An estimate of the magnitude of β and γ can be obtained from Bartlett's[23] theoretical calculation of $C_{\pi\pi\pi\pi}$. While the absolute magnitude of $C_{\pi\pi\pi\pi}$ is not given correctly by this calculation, it is not unreasonable to suppose that the ratios of the values of $C_{\pi\pi\pi\pi}$ at different internuclear distances are fairly well represented. Using Slater's[24] value of the screening constant for the π orbits, one concludes that β and γ are quite small and we have accordingly neglected them in computing the value of $W(C_6H_6)$ given in Table I. It should be emphasized that in computing the energies of molecules such as benzene it is not sufficient to consider merely the interaction between π orbits. It is imperative also to include the forces in the plane of the benzene ring, as we have done. The importance of bond forces in the plane of the ring has been shown by Penney;[7] the importance of the steric terms which appear in W_0 has been discussed above in connection with acetylene. The errors which attach to incomplete treatments which consider only π orbits will be illustrated in the discussion of results.

TABLE I. *Energies of hydrocarbons.*[25]

		Calc.	Obs.
Methane	CH_4	(16.3)v	16.3v
Ethane	C_2H_6	(27.6)	27.6
Propane	C_3H_8	38.9	38.9
Butane	C_4H_{10}	50.2	50.2
Ethylene	C_2H_4	(21.8)	21.8
Propylene	C_3H_6	33.1	33.1
1,2,3,4 tetrahydrobenzol	C_6H_{10}	61.9	61.8
Cyclohexane	C_6H_{12}	67.4	67.1
Acetylene	C_2H_2	14.9	15.2
Benzene	C_6H_6	52.2	52.2
1,2 dihydrobenzol	C_6H_8	56.3	56.7
Naphthalene	$C_{10}H_8$	81.4	82.5

On taking account of the interaction of the four π orbits in 1,2 dihydrobenzol, we find $W_1=3.23\alpha$. For napthalene we have used Sherman's[26] result for the resonance energy. This gives $W_1=9.54\alpha$.

Discussion of Results

The agreement between the calculated and observed energies is remarkably good, much better than one has any right to expect from so crude a theory. It should be pointed out that inclusion, in the H-L-P-S treatment, of non-orthogonality and higher order permutation integrals generally seems to spoil the results of the simple theory.[27] Any agreement obtained by use of the simple theory must consequently be regarded as rather accidental.

It is not at all clear why molecules for which (3) is a good approximation should so nearly obey a bond additivity law. The variation in W_{HC} from molecule to molecule is over $\frac{1}{4}$ v, while $W_v(C)$ varies by almost $\frac{1}{2}$ v. In addition, the hydrogen-hydrogen repulsion energy is often quite large, and it by no means obeys an additivity rule. The situation is not clarified by considering net, rather than gross, bonding energies. For example, the net C–H bonding energy in ethylene is 4.45 v, in ethane 4.04 v, and in cyclohexane 3.95 v. In computing these net bonding energies, the energy of the hydrogen-hydrogen repulsions has been divided equally among the C–H bonds. The energy of the C–C bond in ethane is 3.36 v, and that of the C=C bond in ethylene is 3.77 v. The empirical bonding energies given by Pauling and Sherman[28] are

[22] F. Seitz and A. Sherman, J. Chem. Phys. **2**, 11 (1934); R. Serber, J. Chem. Phys. **2**, 697 (1934).
[23] J. H. Bartlett, Jr., Phys. Rev. **37**, 507 (1931).
[24] J. C. Slater, Phys. Rev. **36**, 57 (1930).
[25] The experimental values have been taken from the following sources: F. D. Rossini, Bur. Standards J. Research **13**, 21 (1934); L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932); and references 14, 28, 30.
[26] J. Sherman, J. Chem. Phys. **2**, 488 (1934).
[27] H. M. James, J. Chem. Phys. **2**, 794 (1934); A. S. Coolidge and H. M. James, ibid. **2**, 811 (1934).
[28] L. Pauling and J. Sherman, J. Chem. Phys. **1**, 606 (1933).

(C−H)=4.07 v, (C−C)=3.15 v, (C=C) =5.56 v. The wide divergences between these values force one to the conclusion that the validity of an empirical bond additivity law is purely fortuitous. The bond additivity rule does, in fact, overstabilize cyclohexane and 1,2,3,4 tetrahydrobenzol by $\frac{2}{3}$ v and $\frac{1}{4}$ v, respectively. The H-L-P-S method thus gives a somewhat better account of the energies of these molecules than the additivity rule, although, of course, the accuracy of our treatment is hardly sufficient to justify the comparison.

Although no general bond additivity rule should be expected to hold for molecules whose energies are given by (3), the theory does predict an additivity relation between the energies of the higher members of the paraffin series, C_nH_{2n+2}. This follows from the fact that the bonding of each added CH_2 group is of the same type, namely Van Vleck's class (a) type, while for $n>6$ the repulsions between the two added H atoms and the H atoms on the two end C atoms become negligible. This agrees qualitatively with the results of Rossini,[26] who finds an additivity relation for the paraffins when $n>5$, but slight deviations for the lower members of the series.

Before discussing benzene, a few words regarding Pauling, Wheland and Sherman's[29] theoretical formulas for resonance energies may not be amiss, since the precise significance of their method of calculation is by no means clear. Thus Hückel[30] has argued that if benzene were considered to have three single carbon-carbon bonds and three double bonds the energy would be $W'=W_0+3\alpha$, whereas solution of the six electron problem would give $W=W_0+2.605\alpha$. The resonance energy $W-W'$ is consequently asserted to be -0.395α, and not 1.105α, as stated by Pauling and Wheland. But this argument is evidently not correct. In fact, we see from (2) or (4) that $W'=W_0+4\frac{1}{2}\alpha$, while (7) gives, on putting $\beta=\gamma=0$, $W=W_0+5.605\alpha$. The difference $W-W'$ has just the value found by Pauling and Wheland. One can readily show that their method will always give the correct resonance energy. The fallacy in the argument to the contrary arises from the fact that it does not properly take into account the steric terms which appear in W_0.

One must carefully distinguish between the theoretical resonance energy and the so-called "observed resonance energy" used by Hückel and by Pauling, Wheland and Sherman. The former is the difference between the theoretical energy obtained by treating the interaction of the π orbits as an n electron problem, and the energy calculated under the assumption of simple electron pair bonding. The latter is taken to be the difference between the observed energy and the energy computed from the empirical bond additivity law: the name "resonance energy" has been applied to this quantity under the supposition that it is equal to the theoretical resonance energy. However, the theory as we have developed it indicates a serious breakdown of the bond additivity law as used for molecules such as benzene. For benzene, we find, under the assumption of simple electron pairing, $W'=-49.2$ v, while the bond additivity law gives $W'=-50.6$ v. For 1,2 dihydrobenzol the corresponding figures are -51.6 v and -56.3 v, and for napthalene -75.9 v and -79.2 v. This failure of the bond additivity law results from the very low value of the theoretical C=C bonding energy for such molecules, 3.77 v, compared to the empirical value, 5.56 v. The theoretical resonance energies for the three molecules are -3.0 v, -4.7 v, -5.5 v, respectively, while the "observed resonance energies" are -1.6 v, -0.4 v,[31] -3.2 v. The "observed resonance energies" appear to have no theoretical significance whatsoever. It consequently seems very difficult to attach any meaning to calculations, such as those of Pauling, Wheland and Sherman, which refer to these quantities.

[29] Pauling and Wheland, reference 18; Pauling and Sherman, J. Chem. Phys. 1, 679 (1933); Sherman, reference 25.

[30] E. Hückel, *Aromatic and Unsaturated Molecules*, International Conference on Physics, London, October, 1934.

[31] It should be noted that the Pauling-Wheland-Sherman procedure predicts a resonance energy, -2.6 v, in definite disagreement with this value.

An Experimental Investigation of the Effect of Pressure on Phase Equilibria of Sodium Tungstate and of Related Thermodynamic Properties

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In order to clarify some uncertainties concerning the physical properties of sodium tungstate the effect of pressure on phase equilibria to 1000 bars, the heats of inversion and of melting, and the specific volume (density) at 30° were determined. Sodium tungstate is trimorphous at atmospheric pressure, form I being stable from 695.5° (melting point) to 588.8°, form II stable from 588.8° to just below 587.6°, and form III stable below this temperature. The I⇌II inversion is estimated to take place at 588.8° with a heat change of 14 joules/gram but no volume change (independent of pressure). Because of the large amount of undercooling in the I→III inversion, the II⇌I transition could be obtained metastably to 613 bars. The III⇌I inversion takes place promptly and reproducibly on heating but not so on cooling, the temperature change being dependent in large measure on the past history of the charge. Heating curve values lead to the expression $t=588.8+0.025(p-40)$ with a heat change of 105 joules/gram and volume change of 0.035 cm³/gram. The triple point lies at $t=588.8°$ and $p=40$ to 80 bars. The II⇌III inversion is very similar in behavior to the I⇌III inversion; here $t=587.6+0.029\ p$ on the heating curve. In order to represent specific volume as a function of temperature from 20° to 1300° the data of Jaeger and of Austin were also utilized. The published density of sodium tungstate was found to be in error and therefore a redetermination was made. The value obtained by us, 5.13±0.01, is 20 percent higher than that given by F. W. Clarke (J. L. Davis). The low-temperature modification expands from 0.195_0 cm³/gram at 30° to 0.203_2 cm³/gram at 587.6°. The salt inverts at this temperature, attaining the volume 0.238_2 cm³/gram, and finally, it again increases in volume at the melting point, 695.5°, to 0.256_5 cm³/gram.

INTRODUCTION

Scope of the investigation

Three crystalline forms of (anhydrous) sodium tungstate are known to exist but the exact relationship between these phases at atmospheric pressure is still somewhat in doubt, no work having been done at other pressures. The temperature-pressure-phase equilibria relations of these three solid phases and of the liquid phase were therefore determined to 1000 bars (10^9 dynes/cm²) pressure. In order to utilize these data to obtain other thermodynamic properties of sodium tungstate the heats of inversion and of melting and the density at 30°C were redetermined. From these data, together with Jaeger's liquid density data and Austin's thermal expansion data from 20° to 500°C, the specific volume could be evaluated as a function of temperature from 20° to 1300°C.

Description of the material used

A pure grade of sodium tungstate was recrystallized either by cooling a hot saturated solution or by precipitating it by the addition of 95 percent ethyl alcohol to a nearly saturated solution. The resulting sodium tungstate dihydrate was dried at 125°, yielding very finely powdered sodium tungstate which, however, was not completely anhydrous.[1] The last traces of water were removed by melting the salt.

Boeke[2] states that the low-temperature modification of sodium tungstate is optically isotropic. The material was found to have a weak birefringence, however, and examination of x-ray powder photographs shows that the symmetry is not that of the cubic system.[3] It has a mean refractive index ($\lambda=547\text{m}\mu$) of 1.678.

TEMPERATURE-PRESSURE PHASE EQUILIBRIA

The three crystalline modifications of sodium tungstate will be designated I, II and III, to denote the high, intermediate, and the low temperature forms, respectively. The liquid phase will be designated as *L*.

Previous work

The results recorded in the literature[4] show that on cooling two breaks are obtained in the

[1] F. Hoermann, Zeits. f. anorg. allgem. Chemie **177**, 150 (1929) states that the dihydrate can be dehydrated at 100°. It was found, however, that material dried at 125° retained up to 0.5 percent of water.

[2] H. E. Boeke, Zeits. f. anorg. allgem. Chemie **50**, 359 (1906).

[3] We are indebted to Mr. C. J. Ksanda of this Laboratory for the x-ray photographs.

[4] The literature to 1929 is given in Gmelin's Handbuch der anorg. Chemie, Wolfram system No. 52, 212 (1933).

curve: (a) a small heat effect in the range between 590° and 576°, and (b) a large heat effect in the range between 583° and 560°. On heating there appears to be only a single arrest at about 588°. Van Klooster and Germs found that if cooling was arrested at 584° there was on subsequent reheating an arrest at 591°. Kracek[5] made further measurements and found that the small heat effect took place at 586° on cooling and that it could be reversed readily, provided the temperature did not fall low enough for the large heat effect to begin, taking place at 592° on reheating. The large heat effect was observed to take place with considerable undercooling, and reheating afterwards gave an apparently single arrest at 588°. This behavior is almost an exact parallel to that of potassium nitrate, and the modifications were accordingly numbered in the Smithsonian Tables to agree with Bridgman's nomenclature for the latter substance,[6] assuming the intermediate form to be metastable at atmospheric pressure. Boeke observed with a heating microscope that the melt crystallizes in birefringent dendritic crystals which transform at 590° to a still more birefringent form and then invert at 584° to become optically isotropic. On reheating, the phenomena are said to occur in reverse order. Boeke's observations would indicate that the intermediate form of sodium tungstate has a temperature range of stable existence at atmospheric pressure instead of coming in metastably as was supposed by Kracek.

The results of this paper establish, among other things, the validity of Boeke's observations, and also show that, with proper technique, both arrests can be observed on heating as well as on cooling.

Experimental procedure

The pressure investigation was carried out in a water-jacketed steel bomb containing a platinum-rhodium resistance furnace. A detailed description of the bomb has been given in an earlier paper.[7] Pressures were measured with a resistance gauge consisting of a hundred ohm coil of manganin wire immersed in the pressure fluid but kept at room temperature (25°). The coil is connected to the apparatus for measuring the resistance through a pressure-tight electrically insulated packing. The sensitivity in measuring changes in resistance (about 0.2 ohm per kilobar) was such that one scale division corresponds to about one bar. The scale for this electrical pressure gauge was calibrated by comparison with an absolute gauge of the free-piston type. The pressure medium used was nitrogen gas.

Temperatures were measured with Pt-PtRh thermocouples. The leads are carried out of the bomb through pressure-tight electrically insulated packings in the bomb lid. The scale for these thermocouples was obtained by calibration at several fixed points and interpolated from the table of L. H. Adams.[8]

The differential temperature, i.e., the difference in temperature between the inert body, in this case silica glass, and the sodium tungstate charge, was measured with PtRh-AuPd-PtRh thermocouples.

The inversion and melting temperatures were obtained from differential heating and cooling curves.

Some of the measurements at atmospheric pressure were made in an ordinary platinum resistance furnace in connection with the calorimetric data.

Experimental results

The accuracy of the determination of the temperature-pressure-phase *equilibrium curves* for the III⇌II and III⇌I inversions is limited by the rather wide passive regions within which the rate of transition is not measurable. The upper bound (heating curve values) of these regions is reproducible to within 0.5°, taking place promptly but not isothermally. The lower bound (cooling curve values), although prompt when initiated, is nevertheless variable and not readily reproducible because it depends in a large measure on the past history of the sodium tungstate charge. It was found that if the powder was first sintered or melted to a cake it would react more or less as a single crystal, i.e., the individual crystalline grains, by this procedure, seem to have been brought into contact intimate

[5] Kracek, Smithsonian Physical Tables, 8th Edition, p. 261 (1933).
[6] P. W. Bridgman, Proc. Am. Acad. **51**, 579 (1916); F. C. Kracek, J. Phys. Chem. **34**, 225 (1930).
[7] Roy W. Goranson, Am. J. Sci. **22**, 481 (1931).
[8] L. H. Adams, Int. Crit. Tab. **1**, 59 (1926).

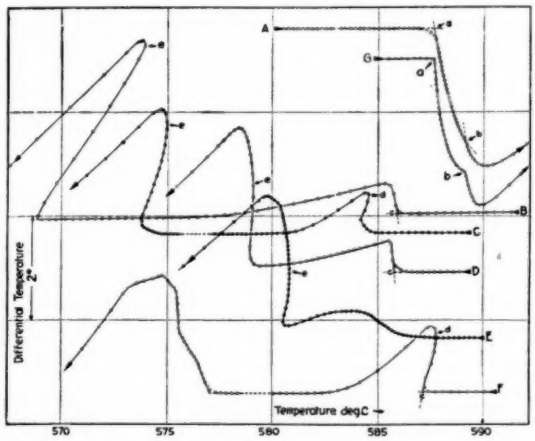

FIG. 1. Typical differential heating (*A*, *G*) and cooling curves (*B* to *F* inclusive) through the two inversions.

enough to initiate the reaction in their neighbors. Moreover, this procedure of first sintering or fusing to a cake increases the thermal conductivity and thereby lessens temperature gradients in the charge; the unfused precipitate, dehydrated at 125°, is an extremely fine powder and a good thermal insulator, and such a charge would therefore have high temperature gradients when heating or cooling. Differential cooling curves yield a lower bound averaging about 6° below the upper bound, and undercooling of as much as 15° has been observed. By repeated reversals of the heating and cooling curves before the transition was complete the undercooling could be apparently largely eliminated, but even with this technique the maximum value obtained at atmospheric pressure for the inversion temperature on the cooling curve was still 5° below the inversion temperature on the heating curve; at 420 bars pressure this technique was able to bring the cooling curve value to within 1° of the heating curve value. The essential characteristics of the differential heating and cooling curves do not vary appreciably with pressure, but the curves do become more reproducible at high pressures, perhaps as a result of increased efficiency in heat transference. Such curves are reproduced in Fig. 1; they represent runs made at one bar pressure, but the shapes of the transition curves are typical of any of the pressure runs. The curves of Fig. 1 were all obtained with the same sample; cooling curves *B* to *F* inclusive demonstrate the variability in values, indicated by "*e*," obtained for the II→III inversion.

TABLE I. *Temperature-pressure relations of the III⇌II and III⇌I inversions.* "*H*" denotes the beginning of inversion on heating and "*C*" the beginning on cooling. The asterisk value is calculated (as shown later in the text).

Pressure in bars	Temperature *H*	*C*	Pressure in bars	Temperature *H*	*C*
1	587.6*		440	598.5	—
1	587.5	581.1	625	603.9	599.4
40	588.8	582.6	715	606.0	598.8
90	589.3	582.7	740	605.5	—
175	592.4	583.6	890	—	605.2
276	594.6	—	923	611.3	—
301	595.5	592.5	990	613.0	606.4
410	599.2	—	1030	614.0	—
418	599.2	597.7			

The experimental results for the III⇌II and the III⇌I inversions are tabulated in Table I.

The II→I inversion, when it follows immediately upon the III→II inversion, is not readily detectable on the differential heating curve because it takes place only one and a half degrees above the beginning of the III→II inversion at atmospheric pressure and with only about one-seventh the heat effect of the latter. With careful technique the break can be obtained (Fig. 1, points "*b*" on curves *A* and *G*) and this break can be easily accentuated by reversing the cooling curve before the II→III transition has been completed. This inversion is prompt but not isothermal; superheating and undercooling of about one-half degree each have been observed for this transition. Because of the large amount of undercooling in the I→III transition it was found that ordinarily the transitions would take place metastably in the order I→II→III up to 613 bars pressure. It was also possible to reverse the cooling curve before the II→III transition occurred and so to obtain the metastable II→I transition up to 300 bars pressure. Typical records of such reversal curves are presented in Fig. 2 and were made in the order as numbered. The metastable prolongation of the I⇌II pressure-inversion curve was therefore determined to 613 bars pressure. The experimental results for the II⇌I inversion are collected in Table II.

The temperature-pressure results given in Table I for the III→I (heating curve values) transition can be represented, within the accu-

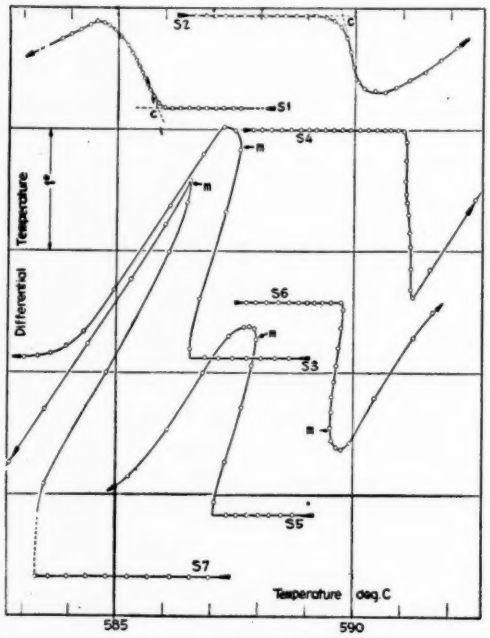

FIG. 2. Typical differential heating and cooling curves of the I⇌II inversion made in the order as numbered without going through the II⇌III inversion.

racy of the experiments, by the slope $dt/dp = 0.025$ or, if no account be taken of stable and metastable states and extrapolated to one bar, by the equation

$$t_{III \to I} = 587.8 + 0.025p,$$

where t denotes temperature in degrees C, and p pressure in bars.

For reasons already given, the cooling curve values (I→III) were not used in the calculation, especially as in a number of the experiments the cooling curve values represent the metastable II→III rather than the stable I→III transition.

TABLE II. *Temperature-pressure relations of the II⇌I inversion.* "*H*" and "*C*" denote the beginning of inversion on the differential heating and cooling curves, respectively.

Pressure in bars	Temperature *H*	*C*	Mean
1	589.5	588.0	588.8
1	589.1	588.5	588.8
40	589.9	588.1	589.0
90	588.6	588.7	588.6
175	588.5	588.8	588.7
276	589.4	587.6	588.4
300	589.5	588.5	589.0
410	—	588.9	588.9
613	—	589.2	589.2

The temperature-pressure curve for the II⇌I inversion, as can be seen by inspection of Table II, is independent of pressure, within the experimental error; that is,

$$t_{II \rightleftharpoons I} = 588.8 + 0.000p.$$

The location of the triple point can be evaluated only within limits from the data available. The intersection of the III→I and the II⇌I curves yields $p = 40$ bars at 588.8°. This must be regarded as the lower pressure limit. The true location of this point depends, obviously, upon the location of the true equilibrium temperature-pressure curve for the III⇌I inversion, and, hence, lies at a somewhat higher pressure. Now, since at 420 bars the III⇌I band was found to be only one degree wide, and if we suppose that this width would persist to lower pressures if the I→III transition could take place without the metastable intervention of the sequence I→II→III, it may be estimated from the data that the upper limiting value of pressure for the triple point is 80 bars at 588.8°. Hence,

Na_2WO_4(I, II, III): $t = 588.8°$

$p = 40$ to 80 bars.

Melting curve

The temperature of melting is taken as the end of melting and the temperature of freezing as the beginning of crystallization or as the maximum where undercooling occurs. The experimental values are presented in Table III.

TABLE III. *Pressure melting of Na_2WO_4.* "*H*" denotes the end of melting and "*C*" the beginning of crystallization. The lower four values denote a single sequence and are used in calculating the slope of the curve.

Pressure in bars	Temperature *H*	*C*	Mean
1			695.5
1	695.0	695.0	695.0
500	705.7	705.4	705.5
706	711.4	712.0	711.7
1040	715.6	716.6	716.1

The pressure-melting relations, where temperature represents the mean of the melting and freezing temperatures, was represented as a least square quadratic passed through the points and is given by the following equation:

$$t_{I \rightleftharpoons L} = 695.5 + 0.0219p - 1.18 \times 10^{-6} p^2,$$

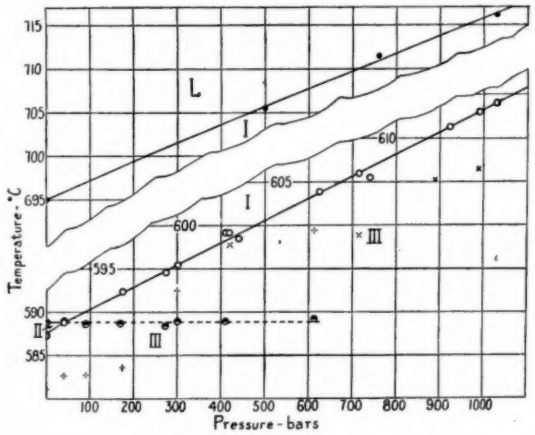

FIG. 3. The temperature-pressure phase diagram of sodium tungstate.

where t is in °C and p in bars.

The temperature-pressure phase diagram for sodium tungstate is given in Fig. 3. Circles with a darkened half-segment represent the I⇌II inversion where t is the mean of heating and cooling curve values except above 300 bars where only cooling curve values could be obtained. The dotted portion of the curve denotes the metastable prolongation of the I⇌II inversion. Open circles represent the III→II and III→I inversion (heating); plusses and crosses represent the values obtained from cooling curves, the crosses denoting the I→III inversion and plusses the II→III inversion. Dark circles represent the means of the melting and freezing temperatures.

CALORIMETRIC DATA

The heats of melting and of the two inversions were measured by the differential heating and cooling curve method described in earlier papers.[9] The values are based on time-differential temperature areas for which calibration of the thermal equivalent of the apparatus was made to 500°. No basic calorimetric data suitable for use with our apparatus (with the possible exception of the value of the heat of freezing of NaCl, which, however, volatilizes so copiously at its melting point as to give very erratic results) exist for the temperature range above 500°, and hence it was necessary to base our determinations on an extrapolation of the thermal equivalent curve beyond this temperature.

The results obtained were as follows:

Liquid⇌Na_2WO_4I,	81	joules/gram
Na_2WO_4I⇌Na_2WO_4II,	14	" "
Na_2WO_4II⇌Na_2WO_4III,	105	" "

Hare[10] has measured the heat of the combined transitions (I–III) by a rather different radiation method which depends upon the absolute evaluation of the radiation constants of the apparatus for each experiment. He obtained 136 joules/gram. It should be noted in this connection, however, that unfused, ignited powder obtained by dehydration of the dihydrate gave for the inversions the values 18 and 123 joules/gram, published by Kracek in the Smithsonian Tables. It was found subsequently that the same filling of the apparatus always gave a larger value with the unfused powder than after the salt had been fused. The discrepancy probably is due to the low thermal conductivity of the original powder. The values given in the tabulation above are for material after fusion. The experimental error is estimated to be ±5 percent.

SPECIFIC VOLUME DATA

Changes of specific volume at the transitions and on melting

From the calorimetric data and the slopes of the transition curves the changes in the specific volume at the transitions can be calculated. The results of such calculations are given in Table IV.

TABLE IV. *Thermodynamic properties of the transitions at atmospheric pressure.*

Transition	Temp. at 1 bar	dp/dt deg/bar	ΔQ joules/gram	Δv cm³/gram
III→II	587.6	*0.029*	105	0.035_0
II →I	588.8	*0.00*	14	*0.00*
I →*L*	695.5	*0.022*	81	0.018_2

For the III→I transition, which is not stable at atmospheric pressure, $dt/dp=0.025$, $\Delta Q=119$ joules/gram, and $\Delta v=0.035_0$ cm³/gram. The temperature of the III→II inversion at atmospheric pressure is calculated to be 587.6°, which agrees with the experimentally determined value.

[9] F. C. Kracek, J. Phys. Chem. **34**, 225 (1930); R. W. Goranson and F. C. Kracek, ibid. **36**, 913 (1932).

[10] A. Hare, Phil. Mag. **48**, 418 (1924).

Specific volume of the liquid

Jaeger[11] has measured the density of liquid sodium tungstate at three temperatures. His values are: 3.685 at 917°, 3.502 at 1128°, and 3.356 at 1330°. A recalculation of these points was made in terms of specific volume yielding the equation

$$v=0.2714+0.703(t-917)10^{-4} \\ -1.423(t-917)^2 10^{-8}$$

where v denotes the specific volume of the liquid which, from this equation, is 0.257 at the melting point.

Specific volume of the crystals at room temperature

The only published value of the density of anhydrous sodium tungstate at room temperature is that by Clarke and Davis,[12] who give 4.1833 at 18.5° and 4.1743 at 20.5°. From these data and those of Jaeger the change in specific volume from solid at 20° to liquid at 695° is calculated to be 0.017. This result is inconsistent with the data of Table IV from which the specific volume change due to the transitions and melting alone is calculated to be 0.053_2. Accordingly, the density at room temperature was redetermined.

The density results on the very fine-grained powder resulting from dehydration of $Na_2WO_4.2H_2O$ clustered about the value 4.82, with deviations of about 0.01, while those on the fused material were in the neighborhood of 5.10, and depended on the grain size, the coarsest size used (10–24 mesh) yielding the highest value. This variability resulted from an imperfect removal of the air trapped in the sample. Consequently the ordinary technique was modified by squeezing toluene (the displacement fluid) into the pores of the grains under a pressure of 6000 bars for about one-half to one hour; this additional treatment increased the measured density by about two parts in 500. Accordingly, the density of sodium tungstate is taken to be 5.13 ± 0.01 at 30°. The corresponding specific volume is 0.195 ± 0.0004 cm³/gram.

[11] F. M. Jaeger, Zeits. f. anorg. Chemie **101**, 183 (1917).
[12] F. W. Clarke (J. L. Davis), Am. J. Sci. (3), **14**, 283 (1877).

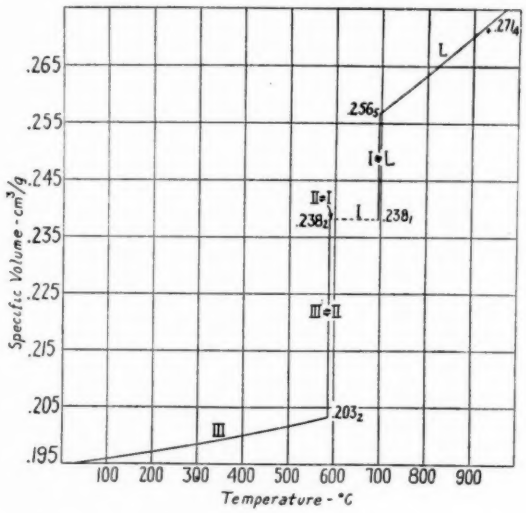

FIG. 4. The specific volume of sodium tungstate as a function of temperature.

Thermal expansion of sodium tungstate

The linear thermal expansion of sodium tungstate has been determined by J. B. Austin[13] from 20° to the inversion temperature. We have calculated a least square quadratic for the volume expansion of modification III from his data to 500° on the assumption that his samples represent aggregates of randomly oriented crystalline grains. The equation is

$$v-v_{20}=v_{20}[53.194(t-20)10^{-6} \\ +41.5(t-20)^2 10^{-8}],$$

which, if the measured value of the specific volume at 30° be inserted, becomes

$$v=0.1947+10.4(t-20)10^{-6}+8(t-20)^2 10^{-9},$$

v denoting specific volume.

Specific volume as a function of temperature

By combining the various data we can finally express the specific volume of sodium tungstate as a function of temperature from 20° to 1300° at atmospheric pressure. In this temperature interval there are two discontinuities, the III→II transition at 587.6° with $\Delta v=0.035_0$ and the $I \rightleftharpoons L$ transition at 695.5° with $\Delta v=0.018_2$. These results are represented graphically in Fig. 4.

[13] We are indebted to Dr. Austin for allowing us to use his results before publication.

The Compressibility of and an Equation of State for Gaseous Ethane

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(Received November 17, 1934)

The compressibility of gaseous ethane (C_2H_6) has been determined from 0.5 to 5.0 moles per liter and from 25° to 250°C with an estimated accuracy of 0.2 percent or better. Above 250°C ethane decomposes at an appreciable rate when confined in steel. An equation of state is fitted to the data. The average deviation of the calculated from the observed pressure is 0.13 atmosphere or 0.21 percent. The equation of state extrapolates to the critical pressure (at 7 moles/liter and 32.1°C) with an error of 10 percent and calculates the weight of a normal liter to 0.2 percent. The vapor pressures of liquid ethane at 0° and 25°C are given.

THE compressibility of the hydrocarbons is of practical as well as theoretical interest. The only hydrocarbon for which extensive modern compressibility data are available is methane, which has been investigated by Keyes and Burks.[1] We have studied the compressibility of gaseous ethane from 25° to 250°C and from 0.5 to 5.0 moles per liter.

The apparatus and the method of procedure have been described in detail elsewhere.[2] A weighed quantity of ethane (approximately 3 grams or 0.1 mole) was confined in a chrome-vanadium steel bomb (of 200 cc volume) which was placed in a thermostat regulated to ±0.001°C, the temperature being measured with a platinum resistance thermometer. The density of the gas was varied and measured by the introduction or removal of known volumes of mercury from a calibrated mercury injector thermostated at 30°C. Pressures were measured on a dead-weight piston gauge. The effect of the temperature of the bomb and of pressure on the volume measuring system was determined experimentally in a blank run in which there was no ethane in the bomb.

The pressures were measured along isometrics as well as along isotherms. At each temperature the method of procedure was to work from the smallest to the greatest gas density and then to check the pressure at the smallest density. At 275° it was found that the pressure had decreased during the course of the measurements, and the pressure corresponding to a given density decreased slowly but steadily with time. Remeasurement of the vapor pressure at 25°C showed an increase in pressure over the previously determined value and also an increase in pressure with decreasing vapor space in the bomb, but no appreciable change with time. This indicates that at about 275° in steel, ethane cracks to give, as one product, hydrogen which rather rapidly diffuses through the walls of the bomb at this temperature. When the bomb was opened, a thin film of an oily tar was found on the inner walls.

Temperatures are given on the international platinum resistance thermometer scale. The strain-free mica-cross platinum resistance thermometer was calibrated at the ice-point (0°), the steam point (100°) and the sulfur boiling point (444.6°) at the beginning and at the end of the measurements. Special hypsometers, which permit very exact calibration at a constant pressure of one normal atmosphere, were used. The maximum difference between temperatures computed from the two calibrations was 0.001°, this maximum occurring at 250°C. Each day the ice-point of the thermometer was determined and correction made for the variation, which amounted at most to 0.002°C during the course of the investigation. The precision of the determination of temperature with one platinum resistance thermometer is about 0.002°C, but the uncertainty of the readings of a single thermometer relative to the international platinum resistance scale increases above 100°C to about 0.01° to 0.02°C at 250°C.

Pressures are given in normal atmospheres. The pressure gauge was calibrated at the vapor

* Contribution No. 335.

[1] F. G. Keyes and H. G. Burks, J. Am. Chem. Soc. **49**, 1403 (1927).

[2] J. A. Beattie, Proc. Am. Acad. Arts and Sci. **69**, 389 (1934).

TABLE I. *Values of the constants of the Beattie-Bridgeman equation of state for gaseous ethane* (C_2H_6).

$$p=[RT(1-\epsilon)/V^2][V+B]-A/V^2$$

$$A=A_0(1-a/V) \qquad B=B_0(1-b/V) \qquad \epsilon=c/VT^3$$

R	A_0	a	B_0	b	c	Mol.wt.
Units: normal atmospheres, liters per mole, °K (T°K = t°C + 273.13).						
0.08206	5.8800	0.05861	0.09400	0.01915	90.00×10^4	30.0462
Amagat units: normal atmospheres, V = 1 at 0°C and 1 atm., °K						
3.69658×10^{-3}	11.9320×10^{-3}	2.6402×10^{-3}	4.2344×10^{-3}	0.8627×10^{-3}	40.543×10^8	30.0462
Berlin units: meters of mercury, V = 1 at 0°C and 1 meter of mercury, °K						
3.70799×10^{-3}	15.7971×10^{-3}	3.4847×10^{-3}	5.5888×10^{-3}	1.1386×10^{-3}	53.510×10^8	30.0462

TABLE II. *Comparison of the pressures calculated from the equation of state with the observed pressures for gaseous ethane.* For each temperature the first line gives the observed pressure and the second line gives the observed minus the calculated pressure. The equation used for the calculated pressures is given in Table I.

Density, moles/liter Temp., °C		0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
		Pressures, normal atmospheres									
25	obs.	11.11	20.14	27.34	32.84	36.88	39.66	41.35			
	obs.-calc.	−0.05	−0.14	−0.19	−0.25	−0.25	−0.16	±0.00			
50	obs.	12.24	22.58	31.24	38.41	44.27	49.02	52.87	55.97	58.49	60.56
	obs.-calc.	−0.02	−0.07	−0.11	−0.11	−0.08	±0.00	+0.15	+0.35	+0.57	+0.75
75	obs.	13.34	24.95	35.08	43.80	51.37	57.98	63.78	68.89	73.52	77.79
	obs.-calc.	−0.02	−0.05	−0.01	−0.02	±0.00	+0.05	+0.11	+0.10	+0.05	−0.12
100	obs.	14.43	27.28	38.79	49.03	58.29	66.68	74.36	81.50	88.25	94.73
	obs.-calc.	−0.03	−0.05	±0.00	−0.01	+0.04	+0.06	+0.05	−0.04	−0.24	−0.61
125	obs.	15.52	29.64	42.49	54.25	65.13	75.26	84.81	93.91	102.73	111.46
	obs.-calc.	−0.03	±0.00	+0.03	+0.06	+0.11	+0.12	+0.08	−0.08	−0.37	−0.80
150	obs.	16.60	31.89	46.08	59.31	71.78	83.61	94.99	106.06	117.00	127.98
	obs.-calc.	−0.03	−0.05	−0.01	+0.02	+0.07	+0.07	+0.02	−0.13	−0.40	−0.80
175	obs.	17.67	34.17	49.66	64.36	78.40	91.93	105.13	118.16	131.20	144.41
	obs.-calc.	−0.05	−0.06	−0.05	+0.02	+0.07	+0.09	+0.06	−0.05	−0.26	−0.58
200	obs.	18.71	36.44	53.25	69.38	84.97	100.19	115.20	130.18	145.30	160.77
	obs.-calc.	−0.09	−0.07	−0.05	+0.01	+0.08	+0.13	+0.14	+0.09	−0.02	−0.18
225	obs.	19.80	38.64	56.73	74.27	91.38	108.24	125.02	141.90	159.08	176.73
	obs.-calc.	−0.09	−0.15	−0.15	−0.10	−0.04	+0.02	+0.06	+0.06	+0.05	+0.01
250	obs.	20.89	40.87	60.23	79.16	97.81	116.30	134.84	153.59	172.87	192.77
	obs.-calc.	−0.08	−0.19	−0.22	−0.18	−0.09	−0.03	+0.05	+0.10	+0.26	+0.44
Average deviation (atm.)		0.049	0.083	0.082	0.078	0.083	0.073	0.072	0.111	0.247	0.477
Average % deviation		0.293	0.276	0.198	0.166	0.151	0.110	0.090	0.140	0.267	0.459

Total average deviation (atm.), 0.131; total average % deviation, 0.213

pressure of liquid carbon dioxide at 0°C for which the value 34.401 normal atmospheres[3] is used. The gauge was recalibrated after the completion of the measurements and showed the normal increase in gauge constant (normal mm of mercury per gram load) with time (0.01 percent per year), for which correction was made. The uncertainty in the determination of pressure is less than 0.05 percent.

Gas volumes at each temperature are expressed in liters per mole and are referred to the specific volume of liquid mercury at the temperature in question and 1 atmosphere. The density of mercury at 0°C was taken to be 13.5955 grams per milliliter and the effect of temperature on the volume of mercury at 1 atmosphere was obtained from the equation given in *International Critical Tables*.[4] At 0.5 mole per liter gas density, the gas

[3] O. C. Bridgeman, J. Am. Chem. Soc. **49**, 1174 (1927).

[4] *International Critical Tables*, Vol. II, p. 457. McGraw-Hill Book Co. Inc., New York, 1927.

volume in the bomb was about 200 cc; at 5.0 moles per liter it was 20 cc. The mercury compressor can be calibrated to ± 0.004 cc at one atmosphere pressure and the uncertainties of the corrections applied for the effect of pressure and temperature on the volume measuring system are about 0.02 cc. Yet the errors in the measurement of volume are larger than these figures indicate, being about 0.1 percent. At each measurement we waited from 1 to 2 hours for equilibrium and usually no change in pressure was observed after the first half hour.

The mass of ethane was determined by weighing in a stainless steel bomb against an almost identical counterpoise. Proper air-buoyancy corrections were made. The accuracy of the determination of mass was 0.01 percent.

The final tabulated pressures are believed to have an accuracy of 0.2 percent or better.

The ethane was obtained from the Linde Air Products Research Laboratory, and guaranteed to be at least 99.9 percent pure. In order to remove any non-condensible gas which might have been present, it was distilled by us three times from one bulb to another by use of liquid air, the first and last portions being discarded. After each distillation the ethane was frozen, and pumped by means of a mercury diffusion pump. It was then loaded into the weighing bottle, weighed, and transferred to the compressibility bomb. That the ethane was of extraordinary purity was indicated by the fact that at 0° the vapor pressure of the liquid remained constant within our experimental error (0.001 atmosphere for relative measurements at constant temperature) while the vapor volume was decreased from 20 to 5 cc; and at 25° the vapor pressure remained constant within the experimental error while the vapor volume was decreased from 40 to 5 cc.

The constants of the Beattie-Bridgeman equation of state[5] were determined from the data. They are given in Table I. In Table II are given the observed pressures and the deviation of the pressures calculated from the equation of state from the observed values. The average deviation is 0.13 atmosphere or 0.21 percent. Although the equation of state gives quite a satisfactory representation of our data, there is one trend in the data that is not reproduced by the equation. The equation requires that the curvature of the isometrics at any temperature increase (numerically) with density. The curvature of the experimental isometrics first increase with increasing density (to about 3.5 moles per liter) and then begin to decrease. In other words the constant c of the equation of state should slowly decrease with increasing density in order that the equation represent this trend in the ethane data.

[5] J. A. Beattie and O. C. Bridgeman, Proc. Am. Acad. Arts and Sci. **63**, 229 (1928).

Vapor Pressures

In the course of our investigation we measured the vapor pressure of liquid ethane at two temperatures. The results are given in Table III.

Table III. *Vapor pressure of liquid ethane.*

Temp.°C	Vapor pressure, normal atmospheres	
	Our values	I.C.T.[6]
0	23.57	23.56
25	41.37	41.5

Weight of a Normal Liter

In Table IV are given the value of the weight of a liter of ethane at 0°C and 1 normal atmosphere calculated from the equation of state, and the observed value. This is not a satisfactory agreement; the difference may be due to the equation which in general gives a low value for the weight of a normal liter for compressible gases (for the gases so far studied the deviation is smaller than in the case of ethane); or to the purity of the ethane used in the measured weights of a normal liter, the suspected impurity (CO_2) giving a high value.

Table IV. *Weight of a liter of ethane at 0°C and 1 normal atmosphere.*

Calculated from the equation of state	1.3535 grams
I.C.T.[7]	1.3566 grams

Calculation of the Critical Pressure

The critical data for ethane[8] are given as 48.8 atmospheres, 0.21 gram per cc (7 moles/liter), and 32.1°C, the critical density being uncertain.

[6] *International Critical Tables*, Vol. III, p. 230.
[7] *International Critical Tables*, Vol. III, p. 3.
[8] *International Critical Tables*, Vol. III, p. 248.

If we substitute the critical temperature and density into the equation of state, we calculate 44.3 atmospheres for the critical pressure, 10 percent lower than the observed value. This should not be considered a bad disagreement since it involves an extrapolation of 40 percent from our highest measured density. It should be pointed out that temperature extrapolations are in general fairly safe but density extrapolations are dangerous. This effect is one that is true of equations of state in general and it is also true of the experimental data. Since the isometrics are so nearly linear, the experimental data can safely be extrapolated over quite a temperature range; but in the region near the critical, the isotherms, no matter what variables are plotted, are too curved to permit extrapolation. That is, from the data in the range 0.5 to 5.0 moles per liter, we cannot predict the data in the region of 7 moles per liter.

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The Critical Constants of Propane

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The critical constants of propane (C_3H_8) are: $t_c = 96.81 \pm 0.01$°C, $p_c = 42.01 \pm 0.02$ normal atmospheres, $v_c = 0.195$ liter per mole (4.43 cc per gram), $d_c = 5.13$ moles per liter (0.226 gram per cc). The uncertainty in the critical volume and density is 1 percent.

IN the course of our measurements of the compressibility of gaseous propane,[1] we investigated a number of isotherms in the critical region and located the critical point. The method used was the same as that employed in the measurements of the compressibility of propane and of ethane,[2] and has been described elsewhere.[3]

Pressures are given in normal atmospheres; temperatures in degrees centigrade on the international platinum resistance scale, and volumes in liters per mole. In the region of the critical point of propane the uncertainties in the measurement of pressure do not exceed 0.03 percent; those in the location of temperature do not exceed 0.005°C; and those in the measurement of volume do not exceed 0.05 percent.

In the determination of the critical data, the purity of the substance is of primary importance. The propane was obtained from the Research Laboratories of the Linde Air Products Company at Buffalo and was stated by Doctor L. I. Dana to be 99.9 percent pure or better. That the propane was of extreme purity is indicated by the measurements of vapor pressure at 50° and 75°C given in Table I. It will be noticed that at 50°C the vapor pressure remained constant within the accuracy of our measurements (±0.001 atmos-

TABLE I. *The effect of varying the vapor volume on the vapor pressure of propane at 50° and 75°C.*

50°C		75°C	
Vapor volume cc	Vapor pressure normal atm.	Vapor volume cc	Vapor pressure normal atm.
93	16.897	50	28.112
62	16.899	35	28.113
46	16.898	26	28.113
37	16.898	15	28.113
31	16.898	11	28.113
26	16.897	9	28.113
23	16.897	7	28.112
20	16.898		
18	16.898		
0.15	16.901		

* Contribution No. 339.

[1] J. A. Beattie, N. Poffenberger and C. Hadlock, to be published shortly.

[2] J. A. Beattie, C. Hadlock and N. Poffenberger, J. Chem. Phys. **3**, 93 (1935).

[3] J. A. Beattie, Proc. Am. Acad. Arts and Sci. **69**, 389 (1934).

TABLE II. *Isotherms of propane (C_3H_8) in the critical region.*

Temp., °C		96.00	96.70	96.80	96.81	96.82	96.90	97.00	97.10	97.20
Density moles/liter	Volume liters/mole				Pressure, normal atmospheres					
4.201	0.2380		41.9030	41.9660			42.0360	42.0995	42.1695	42.2335
4.341	.2304		41.9175							
4.490	.2227	41.3975	41.9280	41.9940			42.0675	42.1360	42.2060	42.2775
4.651	.2150		41.9300	41.9990	42.0075	42.0145	42.0730	42.1445	42.2150	42.2895
4.823	.2073		41.9295	42.0020	42.0095	42.0175	42.0765	42.1515	42.2245	42.3010
4.895	.2043			42.0030	42.0110	42.0190		42.1525	42.2280	42.3040
4.970	.2012			42.0045	42.0115	42.0195		42.1560		
5.008	.1997		41.9300				42.0800		42.2320	42.3090
5.047	.1981			42.0030	42.0120	42.0205		42.1580		
5.126	.1951			42.0040	42.0130*	42.0220		42.1595	42.2370	42.3150
5.208	.1920		41.9290	42.0045	42.0135	42.0235	42.0855	42.1620	42.2400	42.3190
5.293	.1889			42.0060	42.0155	42.0240		42.1655		
5.380	.1859			42.0075	42.0190	42.0260				
5.425	.1843		41.9305				42.0920	42.1725	42.2535	42.3345
5.471	.1828		41.9310	42.0120	42.0215	42.0295				
5.564	.1797		41.9355	42.0200	42.0290	42.0365				
5.661	.1766	41.3965	41.9425	42.0290			42.1105	42.1960	42.2810	42.3640
5.918	.1690	41.3970	41.9865	42.0785			42.1675	42.2575		

* Critical Point

phere) when the vapor volume was decreased from 93 to 18 cc; and that the vapor pressure increased 0.002 to 0.003 atmosphere when the vapor volume was further decreased to 0.15 cc. That is, during a 600-fold decrease in the vapor volume the increase in vapor pressure was practically within our experimental error. At 75°C the vapor pressure remained constant while the vapor volume was decreased from 50 to 7 cc.

In Table II are given the compressibility data on propane in the critical region, the isotherms between 96.7 and 96.9 being plotted in Fig. 1. The pressures are given to 0.0005 atmosphere since relative values are consistent to about 0.001 atmosphere. In the two phase region the densities listed are the average densities of the whole system.

From Fig. 1 it is evident that the critical temperature is 96.81±0.01°C and the critical pressure 42.01±0.02 normal atmospheres. The determination of the critical density cannot be made with so great an accuracy as those of temperature and pressure. The top of the "steam dome" and the inflection point with horizontal tangent of the 96.81°C isotherm agree quite well for a critical volume of 0.195 liter per mole or a critical density of 5.13 moles per liter. The critical volume seems to have been located to ±1 percent. *International Critical Tables*[4] gives $t_c=95.6$°C, $p_c=43$ atmospheres.

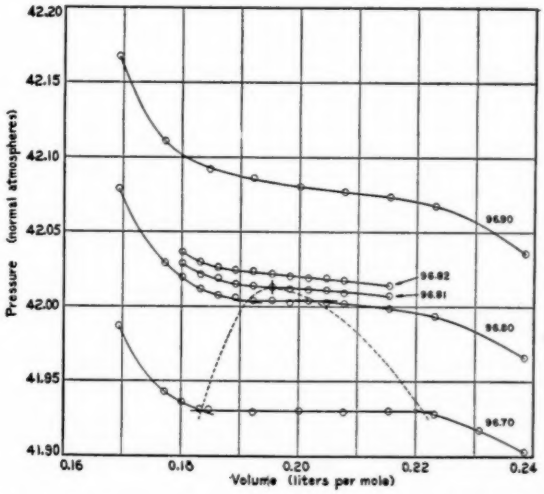

FIG. 1. Isotherms of propane in the critical region. The radius of each circle is 0.002 atmosphere.

[4] International Critical Tables, Vol. III, p. 248. McGraw-Hill Book Co. Inc., New York, 1928.

The Relation Between Vector and Bond Eigenfunction Methods for Spin Degeneracy

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A method previously developed for the calculation of matrix components for problems in which spin degeneracy only is important is shown to be equivalent to an operator method derivable from the vector approach of Dirac. Complete rules for the simple construction of matrices for all possible cases which can arise under these conditions of spin degeneracy are given. An especially simple way of determining secular equations for states of the identical representation is described, and the method is applied to the calculation of the energy of an infinite linear extension of sodium atoms. An inspection method of resolving a crossed six bond eigenfunction in terms of the uncrossed set is given.

INTRODUCTION

RECENTLY Van Vleck[2] and Serber[3] have extended the vector method of Dirac,[4] applying it to the calculation of matrix coefficients of exchange integrals. Van Vleck was chiefly concerned in demonstrating the value of the vector approach in single-atom systems, but indicated its utility in molecular problems. A more generally useful approach to the latter, however, is that employing bond eigenfunctions.[5] This paper considers relations between the vector and bond eigenfunction methods for configurations of orbits in which spin degeneracy only is important. In addition certain improvements in the mechanics of calculation with bond eigenfunctions are described and applied to a consideration of the energy of an infinite linear extension of sodium atoms.

THE VECTOR AND BOND EIGENFUNCTION METHODS

In considering a system of N electrons distributed among an equal number of orbits $a, b, \cdots$ in the many centered field of a molecule or group of atoms one proceeds as follows. A complete set of antisymmetric eigenfunctions is constructed for the configuration in a manner elaborated by Slater.[6] One of these can be written

$$\varphi_i=\frac{1}{(N!)^{\frac{1}{2}}}\sum_P(-1)^p P(a\alpha(1), b\beta(2), \cdots), \quad (1)$$

in which $a\alpha(1)$ expresses the orbit-spin eigenfunction occupied by electron 1, $b\beta(1)$ that of electron 2, and so on. The sum of the P's permutes the electrons in $N!$ ways among the orbit-spin combination orbitals, and $(-1)^p$ is positive for even, negative for odd permutations. There are 2^N eigenfunctions of the type φ_i obtained by taking all possible combinations of the two spin eigenfunctions α or β for each electron. The φ's formed in this manner are all independent, and though in general not orthogonal, they form a convenient set in terms of which we suppose any state arising when perturbations are introduced can be expanded. Because of the method of formation, the φ's are already eigenfunctions of the operator S_z for spin momentum quantized along an optional z axis. A convenient way of expressing all φ's with a particular eigenvalue for S_z is the following:

$$\varphi_r=\frac{Q_r}{(N!)^{\frac{1}{2}}}\sum_P(-1)^p P(a\alpha(1), b\beta(2), \cdots)$$

$$=Q_r\varphi_{\mathrm{I}}. \quad (2)$$

Here φ_{I} is a particular one of the antisymmetric eigenfunctions with the required eigenvalue of S_z. The operator Q_r permutes the spins of φ_{I} with respect to the orbits in such a way as to give rise to a new function φ_r.

[1] National Research Fellow in Chemistry at Princeton.
[2] Van Vleck, Phys. Rev. **45**, 405 (1934).
[3] Serber, Phys. Rev. **45**, 461 (1934).
[4] Dirac, Proc. Roy. Soc. **A123**, 714 (1929).
[5] (a) Slater, Phys. Rev. **38**, 1109 (1931); (b) Kimball and Eyring, J. Am. Chem. Soc. **54**, 3876 (1932); (c) Eyring and Kimball, J. Chem. Phys. **1**, 239 (1933); (d) Pauling J. Chem. Phys. **1**, 280 (1933).
[6] Slater, Phys. Rev. **34**, 1293 (1929).

Frequently it is useful to consider another set of independent functions instead of the φ's. These will be linear combinations of φ's which have the same eigenvalue of S_z:

$$\psi_r=\sum_t c_{rt}\varphi_t=\sum_t c_{rt}Q_t\varphi_1, \tag{3}$$

where c_{rt} is the coefficient of φ_t in the expansion of ψ_r.

If one now applies the perturbations of electron interactions, H, new states arise which can be expanded in terms of the set of ψ's. Perturbation theory then shows that the matrix of $H-W$, for the set of ψ's can be used as a secular determinant whose solutions for W, the energy, when equated to zero will be the required energy levels of the perturbed system. The only matrix components which will be different from zero are those between ψ's with the same eigenvalues for S_z. Hence we can write nonvanishing components as follows:

$$\int\psi_r^*(H-W)\psi_t d\tau=\int\sum_u c_{ru}^*Q_u\varphi_1^* \times(H-W)\sum_v c_{tv}Q_v\varphi_1 d\tau. \tag{4}$$

Consider the integral

$$Q_{rt,\,i}=\int(\sum_u c_{ru}Q_u\varphi_1^*)Q_i(\sum_v c_{tv}Q_v\varphi_1)d\tau. \tag{5}$$

The integrals of the type $\int(Q_u\varphi_1^*)Q_i(Q_v\varphi_1)d\tau$ are unity if $Q_u\varphi=Q_iQ_v\varphi$, otherwise they are zero, providing we neglect non-orthogonality of the orbitals as we shall do here.

The integral, $Q_{rt,\,i}$, defined in (5) is the coefficient of an expression $(K_{Qi}-W\Delta_{Qi})$ in the expansion of (4), where K_{Qi} is an exchange integral between spin-orbit products which differ in permutation of their spins by the permutation Qi. Δ_{Qi} is the corresponding integral with unity instead of H between the spin-orbit products. Because we neglect non-orthogonality of our orbitals $\Delta_{Qi}=0$ unless $i=1$, i.e., unless Qi is the identical permutation. The particular identical permutation Q_1 gives rise to the quantity $(J-W)$, where J is the familiar sum of coulombic integrals. The usual designation of exchange integrals, however, is with respect to a permutation, Pi, of the orbits in relation to the spins, such that for the corresponding integrals we have $P_{rt,\,i}=\pm Q_{rt,\,i}$, the positive or negative sign occurring when the permutation is even or odd, respectively. We have, therefore, the expansion of (4):

$$\int\psi_r(H-W)\psi_t d\tau=(J-W)P_{rt,\,1}+\sum_{Pi}K_{Pi}P_{rt,\,i}. \tag{6}$$

The expression (6) is similar to Eq. (14) of Serber.[3] We can also write (6) in the form

$$\int\psi_r(H-W)\psi_t d\tau=(J-W)I_{rt}+\sum_{i<j}K_{ij}P_{rt,\,ij}, \tag{7}$$

where the subscript ij indicates an exchange between orbits i and j. The quantities I_{rt} and $P_{rt,\,ij}$ are the matrix components of unity and P_{ij} between the states ψ_r and ψ_t. K_{ij} is the exchange integral between the orbitals i and j.

Bond eigenfunctions have the important property of being eigenfunctions of S^2, the operator for the square of the total spin angular momentum, as well as for S_z. They are formed from the antisymmetric functions (φ's) which are eigenfunctions with a particular eigenvalue for S_z.

$$\psi_{a-b\ c-d\cdots}=\sum_u\delta_{ab}\delta_{cd}\cdots\varphi_u,$$

where δ_{ij} is $+1$ for any φ_u which has α on the orbit i and β on j; it is -1 when β is on i and α on j; or it is 0 when both i and j are associated with the same spins. Convenient methods of determining an independent set of bond eigenfunctions have been developed.[7]

In order to work directly with these ψ's which we call bond eigenfunctions it is necessary to have an operator for P_{ij}. Dirac[4] has shown that (in $h/2\pi$ units)

$$Q_{ij}=-P_{ij}=\tfrac{1}{2}(1+4s_i\cdot s_j). \tag{8}$$

Since $2s_i\cdot s_j=(s_i+s_j)^2-(s_i^2+s_j^2)$

and $s_i+s_j=S_{ij}$, $s_i^2=s_j^2=\tfrac{1}{2}(\tfrac{1}{2}+1)=\tfrac{3}{4}$,

we have $2s_i\cdot s_j=S_{ij}^2-\tfrac{3}{2}$.

Here s_i and s_j are the operators for spin vectors

[7] Rumer, Nachr. Ges. Wiss. Gottingen, M. P. Kl., p. 337 (1932).

of electrons i and j, and S_{ij}^2 is the operator for total spin angular momentum associated with the two electrons. As a result of substitution in (8) we find:

$$P_{ij}=(1-S_{ij}^2). \tag{9}$$

Methods have been developed (reference 5c) for operating with S^2 on any antisymmetric function φ_u. These are readily adapted to S_{ij}^2 in the following way. As in the case of S^2,

$$S_{ij}^2=(S_{x,\,ij}-iS_{y,\,ij})(S_{x,\,ij}+iS_{y,\,ij}) +S_{z,\,ij}+S^2{}_{z,\,ij}. \tag{10}$$

Here all operations are to be carried out on the electrons i and j only. The coefficient $h/2\pi$ is omitted on $S_{z,\,ij}$, since we are dealing in $h/2\pi$ units. The i's multiplying $S_{y,\,ij}$ are, of course, the square root of -1.

The effect of the operation $(1-S_{ij}^2)$ on any φ is to interchange the spins of electrons i and j and multiply the result by -1, as is easily verified. Consequently, the effect of P_{ij} in the integral (5) is to pick out from ψ_r and ψ_t the number of times that φ's of the two differ only by a single exchange of spins on the electrons i and j. The negative sign corresponds to the fact that single-exchange integrals occur with signs opposite to that of the coulombic one. These results, of course, were to be expected, but the considerations just stated constitute a simple verification of the vector method of determining matrix coefficients.

One could, of course, proceed to calculate coefficients of exchange integrals occurring in matrix components between bond eigenfunctions by the laborious process expressed in (5) and (9). However, complete and simpler rules have been found already from entirely equivalent reasoning. The reader is referred to previous papers[5c, 8, 9] where methods have been given for determining the coefficients from "sequences," each of which is related to the two bond eigenfunctions of a particular matrix component. The vector method, however, does lead to the interesting comparison with the sequences which follows.

[8] Eyring, Frost and Turkevich, J. Chem. Phys. **1**, 777 (1933).
[9] Stearn, Lindsley and Eyring, J. Chem. Phys. **2**, 410 (1934).

The vector form of the operator P_{ij} suggests rewriting (7) as

$$\int\psi_r(H-W)\psi_t d\tau=(J-W-\tfrac{1}{2}\sum_{i<j}K_{ij})I_{rt} -2\sum_{i<j}K_{ij}(s_i\cdot s_j)_{rt}. \tag{11}$$

We now write the sequence in an equivalent although formally somewhat different form than was used in previous work. Some simple conventions permit us to write the matrix component between two bond eigenfunctions of any multiplicity. Unless the two eigenfunctions are of the same multiplicity, i.e., have the same number of bonds the matrix component is zero. Where they do have the same number of bonds we classify the orbitals in the following way. If two orbitals are bound together in one eigenfunction we put them into two different groups. Now if in the second eigenfunction either or both of these orbitals are bound to new orbitals the new orbitals are assigned to the group not containing the bond partner. This process is continued until the assignment of orbitals starts repeating itself or until a new orbital found is not bound to a partner. If the first case (repetition) arises the two groups are said to form a cycle and in the second case they are said to form a chain. After completing a cycle or chain the process is then repeated with some orbital not yet appearing until all orbitals in the two bonds are classified as cycles or chains. Orbitals not bound in either bond eigenfunction are counted as chains of one link. Any such matrix component can then be written as

$$(-1)^p 2^m[\delta_{u0}\{J-W-1/2\sum_{i<j}K_{ij} +\sum_{m\text{ cycles}}3/2(K_{ij}-K_{ij}')+\sum_{l\text{ odd chains}}(3/2(K_{ij}-K_{ij}') +1/2(K_{ij}''-K_{ij}'''))\} +\delta_{u2}\sum_{u\text{ even chains}}(K_{ij}''-K_{ij}''')]. \tag{12}$$

The symbol δ_{ui} is, of course, 1 if $u=i$, and 0 if $u\neq i$ where u is the number of even chains. For the unprimed exchange integrals, K_{ij}, the i orbital is to be taken from one group in a particular cycle or chain and j is to be taken from the other group. In K_{ij}' both orbital i and j are

to be from the same group. For K_{ij}'' the i and j must be from different chains and if one is from the first group of a chain the other must be from the second group. For K_{ij}''' the i and j must be from different chains and either both from first or both from second groups. It is immaterial which group in a cycle or even chain is counted as first or second. For an odd chain an orbit unbound in either eigenfunction belongs to the first group. This determines the second group. Having chosen the second groups we use them to determine p in the following way. The exponent p is the total number of times that second group orbitals are written as the first letter of a bond in either eigenfunction. J is the sum of the coulombic integrals; W is the energy and $\sum_{i<j} K_{ij}$ is the sum of all possible single exchange integrals. The exponent m is the number of cycles. The justification of (12) is readily obtained along the lines developed in reference (5c) for singlet states. Since for singlet states there are no chains (12) then reduces to $(-1)^p 2^m[M + \sum_{m \text{ cycles}} 3/2(K_{ij}-K_{ij}')$ (13) where the expression has been simplified by making the substitution $M=Q-W-1/2\sum_{i<j} K_{ij}$.

We now give two matrix components as examples of (12). First $\int (ab\ cd\ eg\ f\ h\ ij\ k\ l\ m\ n) \times (H-W)(ac\ bd\ ef\ g\ h\ i\ j\ kl\ m\ n)d\tau = (ad/bc, fg/e, h, m, n, (i/j)(k/l)) = (-1)^4 2^1[il+kj-ik-jl]$. Secondly $\int (ab\ cd\ eg\ f\ h\ ij\ k\ l\ m\ n)(H-W)(ac\ bd\ ef\ g\ h\ ij\ k\ l\ m\ n)d\tau = (ad/bc, i/j, fg/e, h, k, l, m, n) = (-1)^4 2^2[M+3/2\{ab+ac+bd+cd+ij+ef+eg-ad-bc-fg\}+1/2\{eh+ek+el+em+en-fk-fl-fm-fh-fn-gk-gl-gm-gn-kl-km-gh-kn-lm-ln-mn-hk-hl-hm-hn\}]$. In the bond eigenfunctions two letters written with no space between are understood to be bound together. A letter separated by spaces from both neighbors is not bonded. In the first case a is bound to b in the first eigenfunction so they are assigned to different groups in the sequence. Now in the second eigenfunction b is bound to d so they are assigned to different groups and finally in the first eigenfunction d is bound to c. Continuing we simply repeat our letters so that we have the cycle ad/bc. Similarly we have the odd chains fg/e and h and m, etc., and finally the two even chains (i/j) and (k/l). The parentheses are used to distinguish even chains from cycles. The application of (12) to our expression (sequence) which classifies our orbitals into cycles and chains leads immediately to the expanded matrix component. In the expanded form two letters written together signify the corresponding exchange integral between the two orbitals.

The simple ratios between the coefficients of W and the coefficients of the various primed and unprimed exchange integrals K_{ij} in (12) could in fact have been deduced from (11). Remembering that S_z, S_x and S_y have the forms $\begin{pmatrix}1&0\\0&-1\end{pmatrix}1/2$, $\begin{pmatrix}0&1\\1&0\end{pmatrix}1/2$ and $\begin{pmatrix}0&i\\-i&0\end{pmatrix}1/2$, respectively, when written as the matrices operating on the[10] eigenfunctions α and β of S_z. We obtain for the corresponding operators $S_{xi}\cdot S_{xj}$, $S_{xi}\cdot S_{xj}$, $S_{yi}\cdot S_{yj}$ and their sum $S_i\cdot S_j$ operating on $\alpha_i\beta_j$, $\alpha_i\beta_j$, $\beta_i\alpha_j$, $\beta_i\beta_j$ the matrices

$$\begin{pmatrix}1&0&0&0\\0&-1&0&0\\0&0&-1&0\\0&0&0&1\end{pmatrix}1/4, \qquad \begin{pmatrix}0&0&0&1\\0&0&1&0\\0&1&0&0\\1&0&0&0\end{pmatrix}1/4,$$

$$\begin{pmatrix}0&0&0&-1\\0&0&1&0\\0&1&0&0\\-1&0&0&0\end{pmatrix}1/4, \qquad \begin{pmatrix}1&0&0&0\\0&-1&2&0\\0&2&-1&0\\0&0&0&1\end{pmatrix}1/4.$$

Our problem is the comparison of matrix components for twice the last operator with those for the unit matrix for bond eigenfunctions. The subscripts i and j on the spin eigenfunctions α and β are to indicate that these are the spin eigenfunctions associated with the ith and jth orbitals. As we have seen bond eigenfunctions are linear combinations of the antisymmetric configuration eigenfunctions φ_i of Eq. (1) with coefficients of ± 1 or 0. Because of the symmetry of the energy operator H with respect to interchange of electrons we have the well-known equality

$$\int \varphi_u H \varphi_v d\tau = \int (N)!^{\frac{1}{2}} \varphi_u H Q_v(a\alpha(1)b\beta(2)\cdots)d\tau, \quad (13)$$

where $Q_v(a\alpha(1)b\beta(2)\cdots)$ is simply the diagonal element of φ_v. To calculate the coefficient of the

[10] Pauli, Zeits. f. Physik **43**, 601 (1927).

exchange integral ab in (13) we need simply replace H by $-2S_1\cdot S_2$ with a similar procedure for any other coefficient. To calculate the matrix component of unity H is replaced by 1. Now the matrix components for bond eigenfunctions is clearly a sum of terms like (13). An examination yields the following results for the various cases. The coefficients of K_{ij} for cycles arises from the sum of matrix components of the operator $-2S_i\cdot S_j$ for four types of integrals (13) occurring equally often. We give the spin eigenfunctions associated with the ith and jth orbital for both φ_u and φ_v for the four types (1) $\alpha_i\beta_j$, $\alpha_i\beta_i$; (2) $\alpha_i\beta_j$, $-\beta_i\alpha_j$; (3) $-\beta_i\alpha_j$, $\alpha_i\beta_j$ and (4) $-\beta_i\alpha_j$, $-\beta_i\alpha_j$. The only contributions to I_{rt} arises from the first and last of the four pairs so that the ratio $-2(S_i\cdot S_j)_{rt}\div I_{rt}$ is readily seen to be 3/2. For K_{ij} in odd chains two types of integrals are different from zero. Here as in all other cases all integrals occurring at all occur equally often, i.e., 2^m times. The spin eigenfunctions for φ_u and φ_v are $\alpha_i\beta_j$, $-\alpha_i\beta_j$ and $-\beta_i\alpha_j$, $-\alpha_i\beta_j$ so that again $-2(S_i\cdot S_j)_{rt}\div I_{rt}=3/2$. For K_{ij}' in a cycle four types occur $\alpha_i\alpha_j$, $\alpha_i\alpha_j$; $\beta_i\beta_j$, $\beta_i\beta_j$; $\alpha_i\beta_j$, $\beta_i\alpha_j$; $\beta_i\alpha_j$, $\alpha_i\beta_j$ giving a ratio $-3/2$. For K_{ij}' in an odd chain there are the two types $\alpha_i\alpha_j$, $-\alpha_i\alpha_j$ and $-\beta_i\alpha_j$, $\alpha_i\beta_j$ again giving the ratio $-3/2$. For K_{ij}'' between two odd chains we get $\beta_i\alpha_j$, $\beta_i\alpha_j$, giving the ratio 1/2; for K_{ij}''' between two odd chains $\alpha_i\alpha_j$, $\alpha_i\alpha_j$ giving the ratio $-1/2$. Finally for K_{ij}'' between two even chains we have $-\beta_i\alpha_j$, $-\alpha_i\beta_j$ giving zero for the matrix component of I_{rt} and 1 for the matrix component of $-2S_i\cdot S_j$; and for K_{ij}''' we have $-\beta_i\alpha_j$, $-\alpha_i\beta_j$ giving the values 0 and -1 for the respective matrix components. The coefficients in all cases are of course multiplied by the common factor $(-1)^r2^m$.

An additional feature of the present method of calculating matrix coefficients is the ease with which multiple exchange coefficients can be calculated. Any multiple permutation of orbits can always be expressed as the product of single exchanges; for example $P_{ijk}=P_{ki}P_{ij}$. The coefficient of $K_{ijk}-W\Delta_{ijk}$ is most conveniently found by taking advantage of the observation, similar to that used by Heitler,[11] that P_{ij} exchanges the orbits i and j in the bond eigenfunction upon which it operates, changing the sign of the function as well. One can then use $P_{ki}=-1/2\times(1+4s_k\cdot s_i)$ to determine the multiple exchange coefficient after the usual method of sequences. In the second matrix component given consider $P_{abc}=P_{ca}P_{ab}$. Then $P_{ab}(ac\ bd\ ef\ g\ h\ ij\ k\ l\ m\ n)=-(bc\ ad\ ef\ g\ h\ ij\ k\ l\ m\ n)$ determines the sequence with $(ab\ cd\ eg\ f\ h\ ij\ k\ l\ m\ n)$ to be now $-(ac/bd,\ i/j,\ fg/e,\ h,\ k,\ l,\ m,\ n)$, from which $-1/2(1+4s_c\cdot s_a)_{rt}$ is seen to be $2(-1)^4 2^2$. Hence in this instance the coefficient multiplying $(K_{abc}-W\Delta_{abc})$ is 8. More complex changes in the sequence arise when the exchanges involve interchanges of orbits coming from different cycles or from a cycle and a chain, but the procedure is the same.

Singlet Energy Calculations for Symmetrical Systems

Most stable chemical systems are in singlet states, and energy levels of this multiplicity assume particular importance therefore. By combining bond eigenfunctions into new ones in a way indicated by group theory from the atomic configuration, it is possible to factor the singlet secular equation into subdeterminants of smaller degree (for examples see reference 8). Usually, however, one is most interested in the lowest energy level, and then much simpler methods, involving no very great use of group theory, are available. Usually also the lowest level results from solution of the determinant related to the combinations of bond eigenfunctions belonging to the identical representation.

Seitz and Sherman[12] have indicated a fairly simple way to determine eigenfunctions of the identical representation. An equivalent and somewhat simpler method is described by Stearn, Lindsley and Eyring.[9] The expression $\Phi=\sum_R \chi_R R\psi$ where χ_R is the group theory character belonging to the symmetry operation R for a given one-dimensional representation and where ψ is any bond eigenfunction, can be used to determine the required number of Φ's of this symmetry. For the particular identical representation all χ_R's are unity, and the determination of Φ's is extremely simple: $\Phi=\sum_R R\psi$. The procedure is to determine

[11] Heitler, Zeits. f. Physik **79**, 143 (1932).

[12] F. Seitz and Albert Sherman, J. Chem. Phys. **2**, 11 (1934).

all possible Φ's, one from each of the independent set of singlet bond eigenfunctions. Some of the resulting eigenfunctions (Φ's) will be the same, except possibly for sign, while others though different may not all be independent. It is a simple matter, however, to pick out from these an independent set of Φ's.

This procedure can be further improved by drawing the independent bond eigenfunctions on a figure which has the symmetry of the problem under consideration. When this is done it becomes apparent immediately that certain ψ's, with the same pattern of bonds, differ from each other by permitted symmetry operations. These, then, when given the proper sign and summed will form part of a particular Φ, though not necessarily all of it. Certain other eigenfunctions with the same bond pattern will also enter the Φ function, and these additional ones will correspond to "crossed-bond" functions when drawn on the circle of orbits used to determine the independent set. These can be resolved in terms of the independent ψ's, and from all Φ's so found, equal in number to the number of different patterns formed by the independent set when drawn on the figure with the symmetry of the problem, the largest number of independent functions (Φ's) is selected for the construction of the secular equation.

Rules for Resolving Crossed Bond Eigenfunctions

Simple empirical rules for the uncrossing of bond patterns containing as many as five bonds have been given.[13] It is possible in the simple way which follows to extend these methods to twelve-electron eigenfunctions. For these six-bond cases one traces along bonds of the crossed eigenfunction A (never traversing the same bond twice) the shortest connections between the extreme points of the bonds in the uncrossed eigenfunction B. If this is possible the expansion of A contains B at least once. If three or more paths pass through a common point the coefficient of B is $p-2+q$. What is meant by the number of paths p passing through a common point needs to be defined. Frequently parts of the bond lines in A are not traversed in drawing the required shortest paths. All points connected by untraversed lines are for this purpose to be counted as one point. Also any path which passes through a point and which with the perimeter circle separates other paths common to the point into two groups is omitted in determining p for the point. This discarding is continued until there are no more such paths. Since q is zero in cases of five or fewer bonds, it will also be zero when the six bonds of A can be divided into two or more non-intersecting groups. Otherwise q is determined by the number of pairs of diametrically opposite bonds on the perimeter of B which when drawn on A have the following properties. For a given pair to be counted in the determination of q each member of the pair must have its path as drawn on A terminate along two bond lines which cross; the paths for members of such a pair must touch at some point, either directly or by the "shrinking" of untraversed lines as discussed in the previous rules; and the pair members must not be separated by the traced path of another bond, for one or two such pairs q is 1 or 2, respectively. For three such pairs q is 4. Self-explanatory examples are given in Fig. 1.

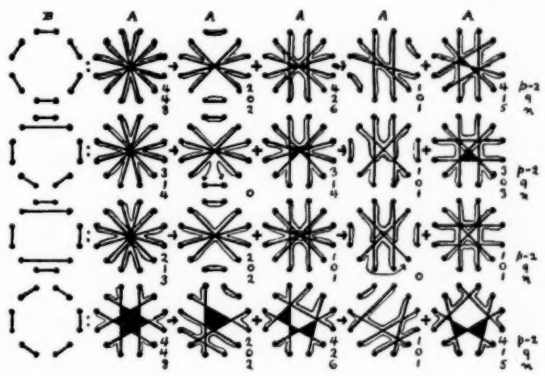

Fig. 1. Examples of the methods of tracing bond paths on crossed-bond eigenfunctions (A) in order to determine the number of times ($n=p-2+q$) a given uncrossed eigenfunction (B) is contained therein. The value of $p-2$ is to be taken as unity for values of $p\leqslant 3$. Filled in areas are those bounded by unused sections of bonds and are to be regarded as essentially points in determining p and q. Pairs of A eigenfunctions connected by plus signs are those obtained by uncrossing one of the crosses of the function immediately preceding the pair.

[13] Eyring and Sun, J. Chem. Phys. **2**, 299 (1934).

Energies for Higher Multiplicities

The method of using bond eigenfunctions drawn on a figure with the symmetry of the actual problem at hand combined with the above rapid method of resolving crossed eigenfunctions thus becomes a simple one for the determination of singlet levels of the identical representation. A similar procedure is valid for levels of higher multiplicity and the identical representation. The method for selecting independent sets of bond eigenfunctions for higher multiplicities follows.[14] Between two of the orbits in the usual circular arrangement one inserts an additional orbit. One then draws non-crossing bonds within the circle, leaving the extra orbit and $\nu-1$ others unbonded, where ν is the multiplicity. If it is possible in a particular eigenfunction to draw lines between the extra orbit and all other unbonded ones without crossing any of the bonds, the eigenfunction is a member of the complete set. After selecting in this manner a complete set, the extra orbit is, of course, discarded. The "pattern" method of determining Φ's as combinations of members of this set can then be applied, but in general the levels thus determined may not contain the lowest level of the system.

Usefulness of Spacial Superposition Patterns

It is possible to use the patterns to determine Φ's belonging to other representations as well if the group theory characters are known. The method is then still superior to an experimental choice of ψ's from which to build the Φ's by use of the symmetry operations and characters. In fact one immediately sees that the Φ's will always be composed of bond eigenfunctions of the same pattern with coefficients depending upon the representation.

Having selected an independent set of Φ's for the problem in hand, one now finds that the use of the patterns is of further value in the calculation of matrix components. For this purpose it is more convenient to use the Φ's expressed in terms of bond eigenfunctions which are of the same pattern, irrespective of whether they are members of the independent set or not. One then, in a manner introduced by Pauling[5d] for orbits arranged in a circle, superimposes bond eigenfunctions upon each other in order to determine matrix components as follows. Suppose Φ_r and Φ_t are the two of the Φ's for which a component is to be determined and ψ_{ru} and ψ_{tv} are typical bond eigenfunctions composing the two, respectively. Then the matrix component $\int \Phi_r \times (H-W)\Phi_t d\tau = \int \sum_u c_{ru}\psi_{ru}(H-W)\sum_v c_{tv}\psi_{tv} d\tau$ is the sum of ones for which coefficients can be found by the sequence method. The superposition patterns of ψ_{ru} and ψ_{tv} are simply diagrammatic ways of writing the sequences, the parts of which will be recognized as follows. Certain "islands" composed of a broken closed line with an even number of bonds are cycles. Unclosed lines of no bonds or of an even or odd number of bonds are chains. First group orbitals are alternate ones starting with the first orbital in an odd chain and any arbitrary orbital in an even chain or cycle (island). The other orbitals belong to second groups. As long as one is dealing with "canonical" eigenfunctions, i.e., those formed according to the previous definition with orbits of each bond written in alphabetical order, it is unnecessary to consider the quantity $(-1)^p$ in (12) as other than positive. The coefficients of J, W, and the exchange integrals are then directly determinable for each superposition pattern from (12). The advantages of the spatial superposition patterns thus employed are that (1) any one of the ψ_{ru}'s, apart from the coefficients c_{ru} and c_{tv}, gives the same types of superposition patterns with all of the ψ_{tv}'s as does any other ψ_{ru}, hence the same coefficients of J, W, and the exchange integrals; and (2) it is possible to allow directly for several exchange integrals being equal as may be indicated by the spacial arrangement of orbits. These factors result in reduction of the labor of calculating matrix components.

The application of the above methods of obtaining eigenfunctions and matrix components for the identical representation from figures drawn according to the symmetry of the problem is particularly simple when the atoms are arranged in one or two-dimensional configura-

[14] Rumer, Teller and Weyl, Nach. Ges. Wiss. Gottingen, M. P. Kl. p. 519 (1932).

tions, such as a straight line, circle, square, etc. Then it is possible to draw an independent set of bond eigenfunctions directly on this configuration, and no symmetry operation on any one of these will give rise to eigenfunctions outside of the complete set. The number of different Φ's is then equal to the number of patterns that arise, and all of them are independent. When three-dimensional figures are necessary no way of determining the independent bond functions directly is possible because of the two-value nature of the spin eigenfunctions. In such cases Φ's will contain bond eigenfunctions other than those of the independent set, and these will need to be resolved in order to pick out independent Φ's.

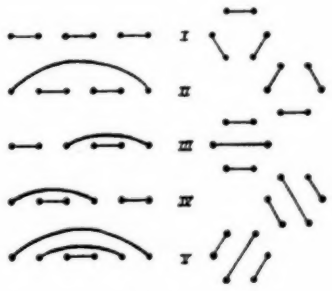

FIG. 2.

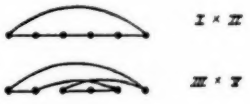

FIG. 3.

ENERGIES OF FILAMENTS OF SODIUM ATOMS

In order to apply the foregoing considerations in a simple way we have calculated the lowest singlet level for the identical representation for various even-numbered configurations of sodium atoms arranged on straight lines or in circles. The object was to find a limiting value for the energy per atom approached as the number of atoms increases. This energy would then be that of a single atom in an infinite linear extension of atoms, a one-dimensional lattice. The circle as well should show the same energy per atom in the limit, and since the circle has the greater symmetry it was hoped that the greater simplification of the secular equations thereby introduced would allow closer approach to the limiting value by permitting determination of energies for larger numbers of atoms. Actually, however, the straight line of atoms more quickly shows a trend which indicates the desired energy in the limit.

In Fig. 2 the independent sets for six atoms are shown as drawn on linear and circular models. The method in the linear case is to draw non-crossing bonds on the line connecting the atoms or to one side of that line. It becomes obvious immediately that a quadratic equation will give the energies for the circle, while one of fourth degree arises for the linear configuration. The Φ's in the circular case are $\Phi_1 = \mathrm{I}+\mathrm{II}$, $\Phi_2 = \mathrm{III}+\mathrm{IV}+\mathrm{V}$; and for the linear model $\Phi_{1'} = \mathrm{I}$, $\Phi_{2'} = \mathrm{II}$, $\Phi_{3'} = \mathrm{III}+\mathrm{IV}$, and $\Phi_{4'} = \mathrm{V}$.

Pauling[5d] has given superposition patterns for the circular configuration, and in Fig. 3 are given several for the linear set. The examples have been chosen to illustrate the existence of apparently different superposition patterns which, however, are easily recognizable as giving the same expansion in terms of the coulombic and exchange integrals. All of the examples given yield $F = 2^1[M + 3/2(5\alpha + 3\gamma + \epsilon) - 3/2(4\beta + 2\delta)]$, where α, β, γ, δ and ϵ are the exchange integrals between orbits or atoms separated, respectively, by 1, 2, 3, 4 and 5 times the distance between adjacent atoms. The matrix component $\int \Phi_{1'}(H-W)\Phi_{2'}d\tau = F$ and $\int \Phi_{3'}(H-W)\Phi_{4'}d\tau = 2F$. The other matrix components are determined similarly.

In this manner the secular equations for circular and linear configurations up to 12 and 8 orbits, respectively, have been set up. These are of twelfth degree for the largest circle considered and of tenth degree for 8 atoms on a line. Beyond these numbers of atoms the determinants are entirely too large to be handled with reasonable labor. We shall not repeat the matrix components here, since the determinants are of limited application.

For estimation of coulombic and exchange integrals we have employed the method previously used in similar investigations.[15, 9] The dissociation energy of the Na_2 molecule, D, is

[15] Taylor, Eyring and Sherman, J. Chem. Phys. 1, 68 (1933).

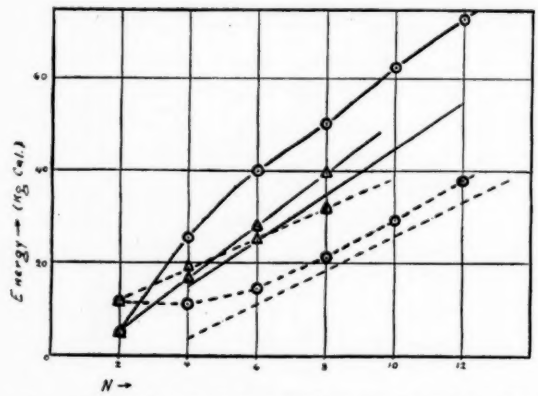

FIG. 4. Energies of various sodium atom configurations. ———Coulombic contributions. – – – – Exchange contributions. ⊙ atoms arranged in circle. △ atoms arranged on line. Curves without circles or triangles after Slater. N is the number of atoms.

17.5 kg cal., $D'=17.7$ kg cal., $\omega_0=159$ cm^{-1}, and $r^0=3.15$A. From these constants a Morse curve was constructed. For the coulombic binding between two atoms at a given distance from each other we have employed Rosen's value[16] of 28.3 percent of the total binding energy as determined from the Morse curve. The corresponding exchange integral then is 71.7 percent of the binding energy. Energies have been calculated only for configurations in which the distance between adjacent atoms is r_0 for the Na_2 molecule. This is sufficiently close to the equilibrium configuration in each case.

TABLE I.

	Circle				Line			
N	J(circle)	$W-J$	W	W/N	J	$W-J$	W	W/N
2			17.7	8.85			17.7	8.85
4	25.6	11.2	36.8	9.20	16.5	19.1	35.6	8.90
6	40.1	14.5	54.6	9.10	28.0	25.4	53.4	8.90
8	50.4	21.3	71.7	8.96	39.5	31.8	71.3	8.91
10	62.6	29.5	92.1	9.21				
12	73.0	38.0	111.0	9.25				

The results are given in Table I and plotted in Fig. 4. It will be noticed that the coulombic and exchange energies for the linear configurations increase by practically constant amounts for each pair of atoms added. Hence the total energy per atom for these cases rapidly approaches the constant value of about 8.91 kg cal., which is the desired limiting energy value. The circular configurations possess greater coulombic energy than do the linear ones. On account of the unusual importance of coulombic energy, the circular arrangements of the atoms appear to be the stabler ones.

The straight lines for coulombic and exchange energy plotted against N for the linear configurations enable one to express the total energy by the following equation:

$$W=5.0+5.7(N-2)+3.2(N+2). \qquad (14)$$

The first two terms arise from coulombic origins, those of the third from exchange contributions. It becomes apparent from (14) that the energy per atom for infinite N is composed of 5.7 kg cal. from coulombic sources and 3.2 kg cal. from electron exchanges.

These results can be compared with those of Slater,[17] who found for an infinite linear lattice of identical atoms to the approximation of including only interactions between adjacent atoms:

$$W=(N-1)J'+0.290(N-3)K, \qquad (15)$$

where J' is the coulombic attraction between adjacent atoms and K the exchange integral between adjacent orbits. By using the values 5.0 and 12.7 for J' and K, respectively, the results of (15) have been calculated for small values of N and plotted in Fig. 3. Though it appears that Slater's equation is not very good for small values of N, it may be written

$$W=5.0(N-1)+3.7(N-3), \qquad (15b)$$

and it then becomes evident that radical differences between (14) and (15b) disappear for large N. At such large values of N the Slater equation indicates somewhat less coulombic energy and a little more exchange energy than the method used here gives, but these differences nearly cancel to give the limiting value for the total energy per atom of 8.7 kg cal. as compared to the 8.9 determined by including interactions between atoms further apart than neighbors. The higher value is, however, greater than the energy per atom in the diatomic molecule, while the lower is not.

[16] Rosen, Phys. Rev. **38**, 255 (1931).

[17] Slater, Phys. Rev. **35**, 509 (1930).

The Activated Complex in Chemical Reactions

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The calculation of absolute reaction rates is formulated in terms of quantities which are available from the potential surfaces which can be constructed at the present time. The probability of the activated state is calculated using ordinary statistical mechanics. This probability multiplied by the rate of decomposition gives the specific rate of reaction. The occurrence of quantized vibrations in the activated complex, in degrees of freedom which are unquantized in the original molecules, leads to relative reaction rates for isotopes quite different from the rates predicted using simple kinetic theory. The necessary conditions for the general statistical treatment to reduce to the usual kinetic treatment are given.

INTRODUCTION

THE customary procedure for calculating bimolecular reaction rates has been to estimate the number of collisions between reacting molecules by using a cross-sectional area taken from measurements on momentum transfer. Such a cross section bears no very clear relationship to the area within which two molecules must fall in order to permit exchange of partners, i.e., to transfer mass. The violence of the collisions is of different orders of magnitude for one thing, and it is quite clear that many collisions which might result in momentum transfer are not oriented properly to permit exchange of atoms. This last difficulty is ordinarily met by introducing an empirical steric or orientation factor to take care of whatever discrepancy may arise between the observed and assumed collision area. This factor is often between 1 and 10^{-1} but may be as small as 10^{-8}.[1] We propose here to obtain explicit expressions for the reaction rates.

The ideas underlying the present calculations are the following ones. The forces between atoms are due to the motion and distribution of electrons and must be calculated, therefore, using quantum mechanics. However, after this is done the nuclei themselves can be assumed to move under the influence of these forces according to classical mechanics. It must be possible, therefore, to calculate the reaction rates by the methods of statistical mechanics (or kinetic theory), if one assumes the aforementioned forces to be known. This is what is done in the present paper using a modification of the schemes developed by Herzfeld,[2] Tolman[3] and Fowler[4] among others and more recently applied in a very interesting way to the ortho-para hydrogen conversion by Pelzer and Wigner.[5]

Cases occur when classical mechanics does not apply to the motion of the nuclei. Zero point energy may be present for some vibrations, and it will be necessary to deal with quantized vibrations in a semi-classical way. Tunneling may occasionally play some role in the motion. In other cases, probably also of very rare occurrence, there may be jumps from one energy level to another. The latter factors may also change the results calculated by neglecting them by orders of magnitude as, e.g., in the case of N_2O.[6] We are not concerned here with reactions in which the last two effects are important.

We now consider in more detail the nature of the surfaces and the motion which corresponds to a reaction. A group of atoms may of course arrange themselves in an infinitely large number of ways. If the energy of such a system of atoms for the lowest quantum state of the electrons is plotted against the various distances between the nuclei, we obtain the potential surface which governs (except in the aforementioned cases) the motion of the nuclei.

Now a system moving on this surface will have kinetic energy which may be quantized for the different degrees of freedom in a variety

[1] Moelwyn-Hughes, *Kinetics of Reactions in Solution*, Oxford Press (1933). W. E. Vaughan, J. Am. Chem. Soc. 55, 4115 (1933).

[2] K. F. Herzfeld, *Kinetische Theorie der Wärme* (Müller-Pouillets Lehrbuch der Physik) 1925.

[3] R. C. Tolman, *Statistical Mechanics*, Chemical Catalog Co., 1927.

[4] R. H. Fowler, *Statistical Mechanics*, Cambridge Univ. Press, 1929.

[5] H. Pelzer and E. Wigner, Zeits. f. physik. Chemie **B15**, 445 (1932).

[6] Volmer and Kummerow, Zeits. f. physik. Chemie **B9**, 141 (1930).

of ways, consistent with the particular energy and the particular position on the surface. Low places in the potential surfaces correspond to compounds. If a particular low lying region is separated from all other low places by regions higher than about 23 kilocalories, the compound will be stable at and below room temperature. The higher the lowest pass the higher is the temperature at which the compound is still stable. A reaction corresponds to a system passing from one low region to another. In thermal reactions the Boltzmann factor makes it certain that the reaction will proceed by way of the lowest pass. The activated state is the highest point along this lowest pass. Before considering the activated state further we discuss the general problem of constructing our partition functions for a given surface.

Formulation of Partition Functions

We here simply sketch the procedure for the gas phase and indicate where the modifications for reactions in solution will come. If a system of atoms is represented by a point on a potential surface such that for the motion in every direction the potential increases or remains constant, we may apply the well-known method of small vibrations to obtain the normal coordinates.[7] Now our system will show translational, vibrational and rotational degrees of freedom. The weighted number of states associated with a degree of translation are

$$\frac{1}{h}\int_0^{l_i} dq_i \int_{-\infty}^{\infty} \exp\left(\frac{-p_i^2}{2m_i kT}\right) dp_i = \frac{(2\pi m_i kT)^{\frac{1}{2}} l_i}{h}$$

where q_i, p_i and m_i are the generalized length, momentum and mass for this degree of freedom, respectively. For a solution or highly compressed gas the integration over the length l_i would involve a potential function in an important way. Also the reacting system would now include in an essential way the degrees of freedom of a certain number of the solvent molecules. If we set the length $l_i=1$ we have the number of unit cells per cm of length, a quantity frequently used in what follows. The other universal constants require no definition. Similarly for a vibrational degree of freedom we obtain for the weighted number of states using classical theory

$$\frac{1}{h}\int_{-\infty}^{\infty} \exp\left(\frac{-p_i^2}{2m_i kT}\right) dp_i \int_{-\infty}^{\infty} \exp\left(\frac{-f_i q_i^2}{2kt}\right) dq_i = \frac{kT}{h\nu_i}$$

where $\nu_i = (1/2\pi)(f_i/m_i)^{\frac{1}{2}}$.

Here f_i and ν_i are the force constant and frequency, respectively. However, summing over the quantized states, we obtain the familiar quantum theoretical expression $(1-\exp(-h\nu_i/kT))^{-1}$ for the weighted number of states for the harmonic oscillator. For $h\nu_i \ll kT$ of course $(1-\exp(-h\nu_i/kT))^{-1} = kT/h\nu_i$. The weighted sum of states for the two degrees of rotation of a linear molecule is

$$\sum_{j=0}^{\infty}(2j+1)\exp\left(\frac{-j(j+1)h^2}{8\pi^2 IkT}\right).$$

Here I is the moment of inertia. Now there are cases for which the position of the activated state on the potential surface depends on the quantum number j. Certain cases of this type will be treated in another place. If the critical configuration does not depend in an important way on j and if $j(j+1)h^2/8\pi^2 I \ll kT$, we can in the well-known way substitute for the summation the integral

$$\int_0^{\infty} 2(j+\tfrac{1}{2})\exp\left(\frac{-(j+\frac{1}{2})^2h^2}{8\pi^2 IkT}\right)dj = \frac{8\pi^2 IkT}{h^2}.$$

For a non-linear molecule we can write for the weighted sum of states the expression $8\pi^2 \times (8\pi^3 ABC)^{\frac{1}{2}}(kT)^{\frac{3}{2}}/h^3$. (If the moments of inertia are small we should sum over the energy levels for a symmetric or asymmetric top.) The expression $\Sigma(2j+1)\exp(-j(j+1)h^2/(8\pi^2 \times (ABC)^{\frac{1}{2}}kT))$ is satisfactory if the moments of inertia differ only a little and the corresponding integral

$$\int_0^{\infty} 4(j+\tfrac{1}{2})\exp\left(\frac{-(j+\frac{1}{2})^2h^2}{(8\pi^2(ABC)^{\frac{1}{2}}kT)}\right)dj$$

yields the classical weighted sum given above.

We now suppose that we have a great number of systems in thermal equilibrium and want to know the relative probability of any system

[7] See, for example, Whittaker, *Analytic Dynamics*, Cambridge Univ. Press, 1927. J. H. Van Vleck and P. C. Cross, J. Chem. Phys. **1**, 357 (1933).

being at points 1 and 2 on a potential energy surface. We assume points 1 and 2 are of such a kind that we know the corresponding normal coordinates and that the energy of point 2 is greater by E_0 than that of point 1. The ratio of the corresponding weighted number of states of points 2 to 1 (which is the relative probability) is obtained by multiplying $\exp(-E_0/kT)$ into the ratio of the product of the weighted sum for each normal mode for point 2 to the corresponding product for point 1. This very brief discussion of the equilibrium constant is sufficient for our purposes. For a rigorous deduction one may consult the work of Fowler previously referred to. The next conception we will require is the rate at which the systems at point 2 are moving along a particular normal coordinate. In our considerations point 2 will in general correspond to the activated state which we now consider in more detail. We call a system at the activated point an activated complex.

The Activated Complex

The activated state is because of its definition always a saddle point with positive curvature in all degrees of freedom except the one which corresponds to crossing the barrier for which it is of course negative. Further, the barriers are so flat near the top that tunneling may be neglected without appreciable error. A configuration of atoms corresponding to the activated state thus has all the properties of a stable compound except in the normal mode corresponding to decomposition and this mode because of the small curvature can be treated statistically as a translational degree of freedom. Thus a non-linear activated complex with n atoms ($n \geq 3$) has three regular translational degrees of freedom corresponding to motion of the center of mass in addition to the one corresponding to passage over the top of the barrier. It also has three rotational degrees of freedom for the molecule as a whole, and the remaining $(3n-7)$ degrees of freedom correspond to internal rotations or vibrations. A linear molecule differs from this in that one of the degrees of freedom which was a rotation is instead a bending vibration. Now the calculation of the concentration of activated complexes is a straight forward statistical problem, given the moments of inertia of the complex and the vibration frequencies. This information is given with sufficient accuracy, even by our very approximate potential surfaces, to give good values for the partition functions.

The procedure for calculating the specific rate is the following: One first calculates the concentration of activated complexes per unit length and with momentum p lying between p and $p+dp$, both these quantities taken for the degree of freedom corresponding to decomposition. This is then multiplied by the associated velocity p/m^* and summed for all values of momenta which correspond to passing over the barrier in the forward direction, i.e., for $p=0$ to ∞. We now formulate the particular expressions for the various cases.

Three Atom Reactions

Consider the reaction

$$A+BC \rightarrow A-B-C \rightarrow AB+C, \tag{1}$$

where the activated complex $A-B-C$ is linear. We write for the specific reaction rate constant

$$k_1 = \left\{ \frac{c g_a i_a \dfrac{(2\pi m_3 kT)^{\frac{1}{2}}}{h^5} \dfrac{8\pi^2 I_3 kT}{\sigma_3 h^2} \prod_{i=1}^{3} \left(1-\exp\left(\frac{-h\nu_i^*}{kT}\right)\right)^{-1} e^{-E_0/kT} \dfrac{(2\pi m^* kT)^{\frac{1}{2}}}{h}}{g_n i_n \dfrac{(2\pi m_1 kT)^{\frac{1}{2}}}{h^5} \dfrac{(2\pi m_2 kT)^{\frac{1}{2}}}{h^3} \left(1-\exp\left(\frac{-h\nu_2}{kT}\right)\right)^{-1} \dfrac{8\pi^2 I_2 kT}{(h^2\sigma_2)}} \right\} \bar{p}/m^*$$

$$= c \frac{g_a i_a}{g_n i_n} \left(\frac{m_3}{m_1 m_2}\right)^{\frac{1}{2}} \frac{I_3 \sigma_2}{I_2 \sigma_3} \frac{h^2}{(2\pi)^{\frac{1}{2}}(kT)^{\frac{1}{2}}} \frac{(1-\exp(-h\nu_2/kT))e^{-E_0/kT}}{\prod_{i=1}^{3}(1-\exp(-h\nu_i^*/kT))}. \tag{2}$$

The subscript 1 refers to atom A, 2 to BC and 3 to the activated complex. E_0 is the difference in energy between the initial substances and the activated state at the absolute zero. The quantities m_j, $I_j\sigma_j$ are the mass, moment of inertia and symmetry number respectively of the particle j. The three frequencies ν_i^* (for $i=1, 2$ and 3) are for the activated complex and ν_2 is the vibration frequency of AB. The letter $g_a i_a$ and $g_n i_n$ are the products of weights arising from electronic states and nuclear spin for the activated and ground state respectively. Frequently $g_a=g_n$ and i_a and i_n need only be considered for reactions in which there is a change in ratio of ortho and para forms. m^* and $\bar{p}$ are the reduced mass and average momentum along the normal coordinate corresponding to decomposition. The quantity in Eq. (2) which multiplies $\bar{p}/m^*$ (the average velocity of activated complex along the normal coordinate corresponding to passing over the barrier) is of course the concentration of activated complex per cm of length normal to the barrier when there is unit concentration of reactants per cc. Now

$$\bar{p}/m^*=\left(\int_0^\infty \exp\left(-p^2/2m^*kT\right)p/m^*dp\right)\Big/\int_{-\infty}^{\infty}\exp\left(-p^2/2m^*kT\right)dp=kT/(2\pi m^*kT)^{\frac{1}{2}}.$$

Thus we see that the terms for the activated complex associated with the normal coordinate along which decomposition occurs give simply $((2\pi m^*kT)^{\frac{1}{2}}/h)\bar{p}/m^*=kT/h$. This factor will of course come in in the same way for every type of reaction.

For some reactions it will happen that the same activated complex may cross the barrier and return without decomposing. This fact reduces the actual reaction rate. It is taken care of by the factor c which is the reciprocal of the average numbers of crossings required for each complex which reacts. It will generally be about unity. There are methods available for estimating the factor c. The other symbols appearing in Eq. (2) are well known and if we introduce our constants in grams cm sec. units, k_1 is given in cc molecules^{-1} sec.$^{-1}$ If we want k_1 in cc moles^{-1} sec.$^{-1}$ we must multiply the k of Eq. (2) by Avogadro's number N.

A form frequently used for writing experimental specific reaction rates is

$$k_2=BT^{\frac{1}{2}}\exp\left(-E/kT\right)=BT^{\frac{1}{2}}\exp\left(-\left(Td\log k_2/dT-\tfrac{1}{2}\right)\right). \tag{3}$$

The activation energy E in (3) is written as $kT^2d\log k_2/dT-\frac{1}{2}kT$ as this is the way it is calculated from the temperature increment.

Putting (2) in the same form as (3) we find for comparison

$$E=E_0+\sum_{i=1}^{3}\left(h\nu_i^*/\exp\left(h\nu_i/kT\right)-1\right)-\left(h\nu_2/\exp\left(h\nu_2/kT\right)-1\right)-kT, \tag{4}$$

and

$$BT^{\frac{1}{2}}=c\frac{g_a i_a}{g_n i_n}\left(\frac{m_3}{m_1m_2}\right)^{\frac{3}{2}}\frac{I_3\sigma_2}{I_2\sigma_3}\frac{h^2}{(2\pi)^{\frac{3}{2}}(kT)^{\frac{3}{2}}}\frac{\left(1-\exp\left(-h\nu_2/kT\right)\right)N}{\prod_{i=1}^{3}\left(1-\exp\left(-h\nu_i^*/kT\right)\right)}$$

$$\times\exp\left\{\sum_{i=1}^{3}\left(h\nu_i^*/kT\right)\left(\left(\exp h\nu_i^*/kT\right)-1\right)^{-1}-h\nu_2/kT\times\left(\exp\left(h\nu_2/kT\right)-1\right)^{-1}-1\right\}. \tag{5}$$

In (5) and in the preceding expressions the masses m_j refer to the masses of a single atom or molecule. If the masses are taken in atomic weight units and written with primes we get:

$$BT^{\frac{1}{2}}=1.41\times10^{12}(300/T)^{\frac{1}{2}}c(g_a i_a/g_n i_n)(m_3'/m_1'm_2')^{\frac{1}{2}}(I_3\sigma_2/I_2\sigma_3)(1-\exp(-h\nu_2/kT))$$

$$\times\prod_{i=1}^{3}(1-\exp(-h\nu_i^{\ddagger}/kT))^{-1}\exp\left\{\sum_{i=1}^{3}(h\nu_i^{*}/kT)(\exp(h\nu_i^{*}/kT)-1)^{-1}\right.$$

$$\left.-(h\nu_2/kT)(\exp(h\nu_2/kT)-1)^{-1}\right\}\text{in cc mole}^{-1}\text{ sec.}^{-1}\text{ units.}\quad(5')$$

For many simple reactions all the terms in $BT^{\frac{1}{2}}$ except 1.41×10^{12} are of the order of magnitude of 1 so that this factor multiplied by the activation energy term gives approximately the rate of the reactions and actually agrees to this approximation with the known experimental values. We here have an exact theoretical collision diameter for reaction rates which replaces the rough kinetic theory value and provides in addition a theory for predicting and explaining divergences.

The inverse dependence on temperature of B is to be noted. This will be the case for molecules for which there are two more fairly stiff quantized vibrations in the activated complex than in the unactivated particles. Partition functions for fairly stiff vibrations depend only slightly on temperature. It is difficult to test this dependence of B upon T experimentally but for this same case there is a predicted dependence of isotopic reactions on mass which may be more readily detected. For the moment of inertia of the activated complex we have $I_3=m_1a^2+m_4c^2-(m_1a-m_4c)^2/m_3$ where m_1 and m_4 are the masses of atoms A and C, respectively, and m_3 is the sum of the masses of the three atoms; a is the distance between A and B, and c the distance between B and C. Now $I_2=m_4m_5d^2/(m_4+m_5)$ where d is the distance between B and C whose masses are, respectively, m_5 and m_4. If all three atoms are alike $I_3/I_2=(a+c)^2/d^2$, i.e., the ratio is independent of the mass of the atoms so that for protium or deuterium mass enters explicitly into B only in the term $(m_3'/m_1'm_2')^{\frac{1}{2}}$. Thus from this cause alone the protium reaction should go faster by a factor of $2^{\frac{1}{2}}$ instead of $2^{\frac{1}{2}}$ as is found if one assumes the only difference lies in the relative velocities of colliding particles. If the two extra bending frequencies in the activated complex are small, the term $(1-\exp(h\nu_i/kT))^{-1}$ approaches the value $kT/h\nu_i$, and remembering that $\nu_i=(1/2\pi)(f_i/m_i)^{\frac{1}{2}}$ where f_i is the corresponding force constant and m_i the reduced mass, we see that B will be dependent upon temperature and depend on mass in the way previously supposed, i.e., $B\sim T/m^{\frac{1}{2}}$. The actual dependence will lie between this extreme and $B\sim1/Tm^{\frac{1}{2}}$. The results of Topley and the present author, soon to be published, indicate that actually the system should more closely approach the latter dependence. These authors have calculated values of B for both the ortho-para-hydrogen conversion and the reaction $Br+H_2$ which agree with experiment.

It should be emphasized that in the particular formulation (2) of our specific reaction rate constant all the quantities may be calculated from the appropriate potential surface which can always be constructed at least approximately. However, in cases where any part of the partition functions is more accurately known from some other source such information can of course be incorporated.

If one realizes that the term $(2\pi mkT)^{\frac{1}{2}}/h$ for a translational degree of freedom has a value of the order of 10^8 for a light atom at ordinary temperature, one sees that the replacement of two terms like this in the initial products by two bending vibrations in the activated complex introduces a factor in k of the order 10^{-16}. This factor is of course the analog of the collision area in the rough kinetic picture and explains why the kinetic picture works approximately, since the other terms in (2), except the average velocity, $\bar{p}/m^*$, are not very different from unity for many reactions. A discussion showing when the general statistical treatment reduces to the usual kinetic theory treatment is given farther on.

In the case where the least activation energy corresponds to a non-linear activated complex the terms

$$8\pi^2I_3kT/(\sigma_3h^2)\prod_{i=1}^{3}(1-\exp(-h\nu_i^{*}/kT))^{-1}$$

in (2) are replaced by the quantity

$$8\pi^2(8\pi^3A^*B^*C^*)^{\frac{1}{2}}(kT)^{\frac{1}{2}}h^{-3}\prod_{i=1}^{2}(1-\exp(-h\nu_i^*/kT))^{-1}.$$

In this case we see a vibrational degree of freedom has become a rotational one. The letters $A^*B^*C^*$ now correspond to the principal moments of inertia of the activated complex. The calculation of the reaction rate and of B and E then proceeds exactly as before.

Four Atoms

Consider the reaction:

$$\begin{array}{c} A-B+C-D\rightarrow A\!\!-\!\!B\rightarrow A-C+B-D \\ \qquad\quad\ \ \vert\quad\ \vert \\ \qquad\quad\ C\!\!-\!\!D \end{array} \tag{6}$$

$$\begin{aligned} k_6 &= cg_ai_a(2\pi m_3kT)^{\frac{1}{2}}h^{-3}8\pi^2(8\pi^3A_3B_3C_3)^{\frac{1}{2}}(kT)^{\frac{3}{2}}\sigma_3^{-1}h^{-3}\prod_{i=1}^{5}(1-\exp(-h\nu_i/kT))^{-1}kT/h\times\exp(-E_0/kT) \\ &\quad\times[g_ni_n(2\pi m_1kT)^{\frac{1}{2}}h^{-3}(2\pi m_2kT)^{\frac{1}{2}}h^{-3}(1-\exp(-h\nu_1/kT))^{-1}(1-\exp(-h\nu_2/kT))^{-1} \\ &\qquad\qquad\times8\pi^2I_1kT\sigma_1^{-1}h^{-2}8\pi^2I_2kT\sigma_2^{-1}h^{-2}]^{-1} \\ &= cg_ai_a(g_ni_n)^{-1}(m_3'/m_1'm_2')^{\frac{1}{2}}(\sigma_1\sigma_2/\sigma_3)1.92\times10^{12}(300/T)(A_3'B_3'C_3')^{\frac{1}{2}}(I_1'I_2')^{-1} \\ &\quad\times\prod_{i=1}^{5}(1-\exp(-h\nu_i/kT))^{-1}(1-\exp(-h\nu_1/kT))(1-\exp(-h\nu_2/kT))\exp(-E_0/kT) \\ &\qquad\qquad\text{in cc mole}^{-1}\text{ sec.}^{-1}\text{ units.} \end{aligned} \tag{7}$$

The subscripts 1, 2 and 3 refer to the species $A-B$, $C-D$ and the activated complex respectively. Primed symbols as before mean that atomic weights are to be used as masses, and atomic weights $\times$(Angstroms)^2 are the units in which moments of inertia are to be given. The significance of the other symbols will be clear from the definitions in connection with Eq. (2). Since all the quantities in (7) are of the order of unity for most reactions except the numerical factor and $e^{-E_0/kT}$ we see again why the kinetic theory picture agrees approximately.

Clearly, for any bimolecular reaction, we can immediately write down the expression corresponding to k_6. If A, B, C and D instead of being atoms are radicals there will simply be additional vibration and internal rotation terms with the expression for moments of inertia of the initial substances in the appropriate cases, taking the form for non-linear molecules. The same reasons for approximate agreement with kinetic theory will remain. Now the activated complex for the type of reactions we are considering is the same for the forward or the reverse reaction. So that in calculating the specific reaction rate constant k for a unimolecular reaction which is bimolecular in the reverse direction we simply modify the denominator of the reverse reaction constant to correspond to the new initial reactants.

Unimolecular Reactions

Suppose we have a non-linear molecule of n atoms decomposing unimolecularly. We then write, cancelling out factors common to the initial and activated states:

$$\begin{aligned} k_8 &= c^*\sigma/\sigma^*(A^*B^*C^*/ABC)^{\frac{1}{2}}\prod_{i=1}^{3n-7}(1-\exp(-h\nu_i^*/kT))^{-1}\prod_{i=1}^{3n-6}(1-\exp(-h\nu_i/kT)) \\ &\qquad\qquad\times(kT/h)\exp(-E_0/kT). \end{aligned} \tag{8}$$

Quantities referring to the activated state in (8) are starred. Now in the particular case where $h\nu_i \ll kT$, i.e., all vibrational degrees of freedom approach a classical behavior we have $(1-\exp \times(-h\nu_i/kT))^{-1}=kT/h\nu_i$ and (7) takes the form:

$$k_0=c^*(\sigma/\sigma^*)\prod_{i=1}^{3n-6}\nu_i\prod_{i=1}^{3n-7}(\nu_i^*)^{-1}(A^*B^*C^*)^{\frac{1}{2}}(ABC)^{-\frac{1}{2}}\exp(-E_0/kT). \tag{9}$$

c^* has the same meaning as the c defined in connection with (2). We of course come to this same result (9) directly if we integrate the appropriate classical expressions for vibration over phase space. Thus for each vibrational degree of freedom:

$$(1/h)\int_{-\infty}^{\infty}\exp(-p^2/(2m_1kT))dp_i\int_{-\infty}^{\infty}\exp(-f_ig_i^2/(2kT))dq_i=kT/h\nu_i$$

if we use the relationship $\nu_i=\frac{1}{2}\pi(f_i/m_i)^{\frac{1}{2}}$. In using (8) it must be remembered that for certain molecules some of the degrees of freedom treated as vibrations can better be treated as internal rotations. In any particular case there is no particular difficulty in doing this. Eq. (9) is sufficiently near to that found for unimolecular reactions at high pressures that there seems no doubt of the wide applicability of both (8) and (9). A formula very similar to (9) was obtained by an approximate method in a paper by Polanyi and Wigner.[8]

General case

Cases could of course be multiplied almost indefinitely but enough examples have been given to leave no doubt of the proposed method of procedure in a particular case. We may write for the specific reaction rate constant for a reaction of any order

$$k_s=c(F_a/F_n)(\bar{p}/m^*)=c(F_a'/F_n)(kT/h)e^{-E_0/kT} \tag{10}$$

where F_a is simply the partition function (or Zustandsumme) for the activated state and F_n is the same quantity for the normal state. F_a' is the partition function for the activated complex for all the normal coordinates except the one in which decomposition is occurring. The partition function for this normal coordinate is included in the factor $(kT/h)e^{-E_0/kT}$. The other quantities have been defined.

The frequently observed negative temperature coefficient of trimolecular reactions has a ready explanation from the point of view presented here. Since the formation of an activated complex from three molecules involves a great loss in entropy, a reaction which goes with a reasonable rate at ordinary temperatures will necessarily have a low activation energy. Further in forming the complex a number of translational and rotational terms with direct dependence on temperature are converted into vibrational terms with very low temperature dependence. Thus the rate will vary inversely with the temperature to a comparatively high power so that if the activation energy is low enough, the k will have a negative temperature coefficient. Kassel[9] has discussed such reactions also.

The extremely low rates, as compared with expectations from kinetic theory, observed in solutions[1] are to be thought of as associated with a change of translational or rotational degrees of freedom of the original molecules into vibrational or oscillational states of the activated complex. These changes may of course be in the enveloping solvent molecule. Any advantage of this formulation of the problem for solutions over any other consideration of entropy and heat content must come from a happy choice of the mechanism of reaction.

When the rate determining step shifts to the collision process as it does for "unimolecular reactions" at low enough pressure we again use well-known statistical methods, but our slow process is now connected with energy transfer in collision.

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[8] M. Polanyi and E. Wigner, Zeits. f. physik. Chemie **A** (Haber Band), 439 (1928).
[9] L. S. Kassel, J. Phys. Chem. **34**, 1777 (1930).

Kinetic Theory Diameters

It becomes a matter of considerable interest to show under what circumstances the preceding general statistical method reduces to the simple kinetic theory scheme as ordinarily applied. We first calculate the number of collisions between two kinds of hard spheres A and B with radii r_1 and r_2 and masses m_1 and m_2, respectively. We use our general method. The respective concentrations per cc of A and B are N_1 and N_2. Our procedure is to calculate the number of pairs of molecules per cc per second which come closer to each other than $(r_1+r_2+\epsilon)$. We then let ϵ approach zero. Our collision complex then has three degrees of freedom associated with translational motion of the center of gravity; one degree corresponding to relative translation along the line of centers; and two degrees corresponding to motion perpendicular to the line of centers, i.e., two degrees of rotation. Before collision there are six translational degrees of freedom, i.e., three for each sphere. The expression for the number of collisions when there is one molecule of each kind per cc may then be written at once:

$$k_{11}=\frac{[(2\pi(m_1+m_2)kT)^{\frac{1}{2}}/h^3]\sum_0^\infty(2j+1)\exp(-j(j+1)h^2/8\pi^2IkT)(kT/h)}{[(2\pi m_1kT)^{\frac{1}{2}}/h^3][(2\pi m_2kT)^{\frac{1}{2}}/h^3]}. \tag{11}$$

The significance of each term will be clear from our previous discussion.

Now if the temperature is not too low we have $j(j+1)h^2/8\pi^2I \ll kT$; so that we can make the usual approximation for the two rotational degrees of freedom, i.e.,

$$\sum_0^\infty(2J+1)\exp(-j(j+1)h^2/8\pi^2IkT)=8\pi^2IkT/h^2.$$

Also kT/h is just the term $[(2\pi m^*kT)^{\frac{1}{2}}/h]\bar{p}/m^*$ of course. The moment of inertia $I=(m_1m_2/m_1+m_2)\times(r_1+r_2)^2$, so that we have after simplification

$$k_{11}=2(r_1+r_2)^2(2\pi kT(m_1+m_2)/m_1m_2)^{\frac{1}{2}}. \tag{12}$$

The number of collisions per cc per second is then

$$Z=N_1N_2k_{11}=2N_1N_2(r_1+r_2)^2(2\pi kT(m_1+m_2)/m_1m_2)^{\frac{1}{2}} \tag{13}$$

which is the usual expression for the number of collisions. Our method of treatment of collisions neglects certain of the refined features arising from the wave nature of the atoms. These are not of interest to us in our present treatment of reaction rates since here we make no explicit use of kinetic theory diameters. For an exposition of these features see a series of papers by Massey and Mohr.[10] For identical colliding systems a symmetry number should be included in (11) to (13).

It is now easy to see when we are justified in using the simple kinetic picture. If the two colliding molecules have (a) none of their internal frequencies appreciably modified in the activated state and (b) if the two degrees of freedom replacing translation, which are not themselves translation, correspond to a rotation (as in the very special case of two colliding atoms) or if they are bending frequencies with force constants of practically zero, then we are justified in applying the simple kinetic theory. Even then there will be some difference arising from the fact that (r_1+r_2) for transfer of momentum is in extreme cases as much as 2.5 times as large as for the corresponding activated complex. Thus approximate agreement with simple kinetic theory will occur in particular cases, but much lower as well as higher values are to be expected in other reactions.

In general it does not seem useful to separate our formulas into a collision factor and a steric factor, but if this is to be done we should associate the kinetic theory diameter with the changes occurring in the particular six degrees of freedom which correspond to translation before the molecules collide. The changes in the other degrees of freedom would then be interpreted as the steric factor. It is

[10] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. **A141**, 434 (1933); **A144**, 188 (1934) and subsequent papers.

interesting to note that if the two bending frequencies arising from translational terms are stiff enough so that the system lies almost entirely in the corresponding lowest states, the reaction diameter as just defined will be less than the kinetic diameter by the factor $8\pi^2IkT/h^2$ which may reach value of the order of 100 for heavy atoms and moderately high temperatures.

The present formulation of the calculation of absolute rates of chemical reactions has certain features in common with a number of more intuitive previous treatments,[11] but has more in common with the treatment of Pelzer and Wigner. It goes beyond these in formulating the general problem in a way susceptible to treatment with our present potential energy surfaces and in pointing out the consequences of quantization on the temperature coefficient and the difference in rate for isotopes. The fact that the activated complex is much like any other molecule except in the degree of freedom in which it is flying to pieces makes possible our comparatively simple formulation. A number of investigations are now in progress in which the absolute rate of reaction is being calculated.

I want particularly to thank Dr. Bryan Topley for valuable discussions as it was with him the present calculations of absolute rates were begun. I also want to thank Professors Taylor and Webb for helpful discussions.

[11] W. H. Rodebush, J. Chem. Phys. **1**, 440 (1933); V. K. La Mer, ibid. **1**, 289 (1933); O. K. Rice and H. Gershinowitz, ibid. **2**, 853 (1934).

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Thermodynamic Functions of Tetramethylmethane[1]

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The Q-sum corresponding to La Coste's eigenvalues for the rotational levels of tetramethylmethane has been expressed by the usual asymptotic expansion. The relatively large coupling terms between the various rotations cancel almost exactly in the Q-sum, so that the thermodynamic functions are scarcely affected by the coupling.

LA COSTE[3] has given an exact solution for the rotational wave equation of tetramethylmethane with zero potential energy. The energy levels are

$$E=(h^2/8\pi^2I_0)[j(j+1)+(I_0/I_s)(m_1^2+m_2^2+m_3^2+m_4^2)+q^2-2qm_\varphi], \quad (1)$$

where I is the moment of inertia of the molecule with methyl groups fixed, I_s the moment of a methyl group about the $C-C$ axis, $I_0=I-(4/3)I_s$ and

$$q^2=m_1^2+m_2^2+m_3^2+m_4^2-(2/3)(m_1m_2+m_1m_3+m_1m_4+m_2m_3+m_2m_4+m_3m_4). \quad (2)$$

The quantum numbers m_1, m_2, m_3 and m_4 of the single methyl groups take integral positive and negative values, while j, m_φ and m_χ are the ordinary quantum numbers for a symmetrical top. The term q^2 within the bracket represents a coupling between the various internal rotations which raises the energy levels and thus decreases the Q-sum. The term $-2qm_\varphi$ splits the levels without shift in their center of gravity and hence raises the Q-sum. Each of these effects is quite large, but the two will be found to cancel almost exactly.

With the notation

$$\sigma=h^2/8\pi^2I_0kT, \quad (3); \quad \rho=I_0/I_s, \quad (4)$$

the Q-sum is

$$Q=\sum_j\sum_{m_\varphi}\sum_{m_\chi}\sum_{m_1}\sum_{m_2}\sum_{m_3}\sum_{m_4}\exp[-j(j+1)\sigma-\rho\sigma(m_1^2+m_2^2+m_3^2+m_4^2)-q^2\sigma+2qm_\varphi\sigma]. \quad (5)$$

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[3] La Coste, Phys. Rev. **46**, 718 (1934).

The term $e^{2qm_\varphi\sigma}$ may then be expanded as a power series, and each term replaced by its mean value over the range $m_\varphi = -j$ to $+j$, by the exact relations

$$\overline{m^2} = (1/3)j(j+1), \tag{6}$$

$$\overline{m^4} = (1/5)j^2(j+1)^2 - (1/15)j(j+1), \tag{7}$$

$$\overline{m^6} = (1/7)j^3(j+1)^3 - (1/7)j^2(j+1)^2 + (1/21)j(j+1). \tag{8}$$

Averages over odd powers naturally vanish. The sums over j, m_φ and m_χ may now be executed at once, using Eqs. (34), (36), (39) and (43) of a previous paper.[4] At this stage the result is

$$\begin{aligned} Q = \sum_{m_1}\sum_{m_2}\sum_{m_3}\sum_{m_4} \pi^{1/2}\sigma^{-3/2}e^{\sigma/4}[1 &+ (\sigma - \sigma^2/6)q^2 \\ &+ (\sigma^2/2 - \sigma^3/6 + 7\sigma^4/360)q^4 + (\sigma^3/6 - \sigma^4/12 \\ &+ 7\sigma^5/360 - 31\sigma^6/15120)q^6 + \cdots] \\ &\times \exp[-\rho\sigma(m_1^2 + m_2^2 + m_3^2 + m_4^2) - q^2\sigma] \\ = \sum_{m_1}\sum_{m_2}\sum_{m_3}\sum_{m_4} \pi^{1/2}\sigma^{-3/2}e^{\sigma/4}[1 &- (1/6)\sigma^2q^2 \\ &+ (7/360)\sigma^4q^4 - (31/15120)\sigma^6q^6 + \cdots] \\ &\times \exp[-\rho\sigma(m_1^2 + m_2^2 + m_3^2 + m_4^2)]. \end{aligned} \tag{9}$$

The final sums are quite readily obtained, using the asymptotic expansion

$$\sum_{-\infty}^{\infty} e^{-\alpha m^2} = \pi^{1/2}\alpha^{-1/2} \tag{10}$$

and its derivatives with respect to α. All sums of the type $\sum_{-\infty}^{\infty} m^{2n+1}e^{-\alpha m^2}$ vanish identically. The result is

$$Q = \pi^{5/2}\rho^{-2}\sigma^{-7/2}e^{\sigma/4}[1 - (1/3)\rho^{-1}\sigma + (7/54)\rho^{-2}\sigma^2 - (62/945)\rho^{-3}\sigma^3 + \cdots]. \tag{11}$$

[4] Kassel, J. Chem. Phys. **1**, 576 (1933).

Since $\rho = 31.54$,[5] the factor in brackets is approximately $1 - 0.01\sigma + 0.001\sigma^2$ and is thus much less important than $e^{\sigma/4}$, the correction term which carries over from the ordinary rigid top. Both factors may be discarded above 100°K, where $\sigma = 0.00220$. The limiting high-temperature value is then

$$Q = \pi^{-1}(8\pi^3 kT/h^2)^{7/2}I_0^{3/2}I_s^2 \tag{12}$$

and, apart from symmetry and nuclear spin corrections,

$$S = R[(7/2) + \ln \pi^{-1}(8\pi^3 kT/h^2)^{7/2}I_0^{3/2}I_s^2]. \tag{13}$$

Also, of course, $H = (7/2)RT$ (14)

and $C_p = (7/2)R.$ (15)

When symmetry and nuclear spin are taken into account, the limiting high-temperature value of Q is multiplied by $2^{12}/3^4 \times 12 = 1024/243$.[6] The effect on the asymptotic expansion is not in all cases quite this simple and cannot very easily be calculated. It is quite certain that the use of this factor is justified above 100°K. Deviations of the rotational specific heat from $(7/2)R$ will then be due to a potential energy associated with the internal rotation, and might be used as an experimental approach to the problem of determining this potential.

The limiting equation (13) agrees with the general equation tentatively proposed by Halford[7] except for the occurrence of I_0 instead of I, the slightly large total moment of the rigid molecule. For ethane, Halford's equation agrees with the calculation of Mayer, Brunauer and Mayer[8] only if the external moments are taken to be A, A and C, where the moments of the rigid molecule are A, A and $2C$. A correction of this nature to the external moments will always be necessary, but ethane is perhaps the only case in which it is not small.

[5] This is calculated with $d_{CC} = 1.54 \times 10^{-8}$ cm and $d_{CH} = 1.08 \times 10^{-8}$ cm.

[6] Cf. Ludloff, Zeits. f. Physik **57**, 227 (1929).

[7] Halford, J. Chem. Phys. **2**, 694 (1934).

[8] Mayer, Brunauer and Mayer, J. A. C. S. **55**, 37 (1934).

The Structure of Caesium Enneachlordiarsenite, $Cs_3As_2Cl_9$

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$Cs_3As_2Cl_9$ is shown to have a hexagonal unit of structure with $a_0=7.37$A, $c_0=8.91$A, containing one molecule. The atomic arrangement is based upon closest-packing of caesium and chlorine, with $D_3^2-C\,3\,2$ as the most probable space-group, but the amount of distortion from the closest-packed positions is not large enough to permit of the unambiguous elimination of $D_{3d}^3-C\,\bar{3}\,m$. A structure based upon D_3^2 accounts well for observed intensity data. Arsenic is shown definitely by the intensity data to have only a pseudo-coordination number of six, and the structure may be qualitatively described as containing $AsCl_3$ molecules embedded in an environment of caesium and chloride ions in such a way that all large atoms fit into an approximately closest-packed arrangement. This is the first structure of this type to be discovered. The ratio of 3Cl per Cs is a particularly happy one for structures of this kind, and a study of this structure gives much insight into the existence and stability of the related group of compounds discussed in the Introduction.

INTRODUCTION

A NUMBER of compounds with the type formula $A_3B_2X_9$ in which A may represent caesium or rubidium, B arsenic or antimony, and X chlorine, bromine, or iodine were originally prepared and described by Wheeler.[1] These compounds crystallize with some form of threefold or sixfold symmetry, or in some cases with only a close approximation thereto. The crystallographic data indicate that two or more essentially distinct but probably closely related structural types are represented. Two points seem of particular interest: (1) How can we account for the existence and stability of these apparently complicated compounds, and (2) what sort of bonding and coordination properties should we ascribe to arsenic (or antimony)? In order to answer these questions, we have made an x-ray study of caesium enneachlordiarsenite, $Cs_3As_2Cl_9$, resulting in a determination of the atomic arrangement existing within the crystal. We have found from x-ray data that two compounds of similar formula, $Cs_3Tl_2Cl_9$ and $Cs_3Tl_2Br_9$, first prepared by Pratt,[2] belong to quite a different structural type.[3]

DETERMINATION OF THE STRUCTURE

Following the directions of Wheeler, crystals of $Cs_3As_2Cl_9$ were prepared in the form of thin, six-sided, optically uniaxial plates somewhat less than one mm in diameter. Laue and oscillation photographs were prepared using, respectively, general radiation from a tube with tungsten target operated at a peak voltage of about 50 kv, and K-series radiation from a tube with water-cooled molybdenum target.

Application of the Bragg formula to the observed spacings of the equatorial reflections from the basal plane appearing upon oscillation photographs gives a value for $d_{(00\cdot1)}/n_1$ of 8.910 $\pm$0.020A, spectra from a cleavage face of calcite being used as a comparison standard. Application of the Polanyi equation, $s\lambda=I\sin\mu$, to observed spacings of layer lines on these photographs leads to identity distances along the axes of oscillation of about 7.4A and 12.8A ($=\sqrt{3}\cdot 7.4$A) accordingly as the axis of crystallographic description (using hexagonal axes) or a direction making an angle of 30° with it is chosen as the axis of oscillation. The data from three completely indexed Laue photographs taken with the x-ray beam inclined at various small angles to c are completely accounted for on the basis of a hexagonal unit with $a_0=7.37$A, $c_0=8.91$A; for no observed reflection gives a calculated value of $n\lambda$ less than 0.24A, the short wavelength limit of the radiation employed. On one photograph, for example, a total of about 135 spots appear with more than 40 forms reflecting in the first order; and in no case is a spot of doubtful nature observed, so that this unit may be confidently accepted as the true one. Reflections from (10·0) and (11·0) obtained by transmission through the very thin plate-like crystals lead to values for a_0 of about 7.4A. Inasmuch as these

[1] Wheeler, Am. J. Sci. **146**, 88 (1893); **146**, 269. See also Groth, Chemische Krystallographie, Engelmann, Leipzig, 1, 434 (1908).
[2] Pratt, Am. J. Sci. **149**, 397 (1895).
[3] Unpublished material.

reflections were too wide for accurate measurement, we have preferred to use Wheeler's apparently reliable value of 1.209 for c_0/a_0 in conjunction with our value of 8.91A for c_0, thus leading to $a_0=7.37$A.

With one molecule of $Cs_3As_2Cl_9$ within the unit cell, the calculated density is 3.42 g/cc, somewhat greater than that of methylene iodide. As we had only a small amount of material, no convenient method of determining the density experimentally was available, but inasmuch as the calculated value lies within the limits to be anticipated, we conclude that we have to deal with a one-molecule unit. As we shall show, all other evidence supports this conclusion.

A Laue photograph with the x-ray beam accurately perpendicular to the basal plane shows no deviation from the threefold axis and three planes of symmetry of D_{3d}. A number of first-order reflections of the types $\{mo\cdot l\}$ with l odd and $\{mm\cdot l\}$ with l odd appearing on Laue photographs together with the observation that $\{00\cdot 1\}$ is not thirded eliminates all space-groups with special criteria.[4] As a_0 is found to lie along a twofold axis and 30° from a symmetry plane, there remain as possible space-groups $C_{3v}^1-C\,3\,m$, $D_3^2-C\,3\,2$, and $D_{3d}^3-C\,\bar{3}\,m$, with no conclusive evidence at this stage to enable us to decide upon one of them. We are able, however, to proceed with a structural determination based upon convincing premises, and leading to the selection of D_3^2 as the probable space-group.

The radius[5] of Cl^- (for coordination number six) is 1.81A. A hexagonal unit of three layers made up of 12 spheres of this size in closest-packing would have $a_0=7.24$A, $c_0=8.86$A. The radius of Cs^+ is 1.69A, but little less than that of Cl^-, and our unit cell contains $3Cs^+$ and $9Cl^-$. Comparing our lattice constants of $a_0=7.37$A, $c_0=8.91$A with those above, the conclusion seems inescapable that the structure of $Cs_3As_2Cl_9$ is based upon a nearly closest-packed arrangement of caesium and chloride ions. Furthermore, if we make the additional and quite reasonable requirement that two caesium ions shall not be in contact with each other, it is not difficult to see that we are led to a unique distribution (excepting small distortions) of the $3Cs^+$ and $9Cl^-$ within the unit cell. This ideal or undistorted arrangement is made up of three identical layers, and may be conveniently symbolized as follows: Let A represent a closest-packed layer with Cs^+ at 00, B a layer with Cs^+ at $\frac{1}{3}\frac{2}{3}$, and C a layer with Cs^+ at $\frac{2}{3}\frac{1}{3}$. The sequence of layers along c is then $ABCABC\cdots$, corresponding to cubic closest-packing. (See Figs. 1–3.) The face-centered unit cube, containing 4 spheres, has Cl^- replaced by Cs^+ at the corners. We note that the rhombohedral angle[6] α for $Cs_3As_2Cl_9$ is 90° 30′, which is indicative of the small amount of distortion of the structure from cubic closest-packing.

Taking layer A at $z=0$, we first place arsenic in $\frac{1}{3}\frac{2}{3}\frac{5}{6}$, $\frac{2}{3}\frac{1}{3}\frac{1}{6}$, at the centers of octahedra of chlorine atoms in positions such that arsenic atoms remain far apart one from another, and also well-removed from caesium ions. The resulting arrangement is obtainable from each of the three space-groups which must be considered, in each case with highly specialized values of a number of parameters. Moreover, a comparison of calculated structure factors for this structure with observed intensities for the various orders of $(00\cdot 1)$, $(10\cdot 0)$, and $(11\cdot 0)$ make it appear

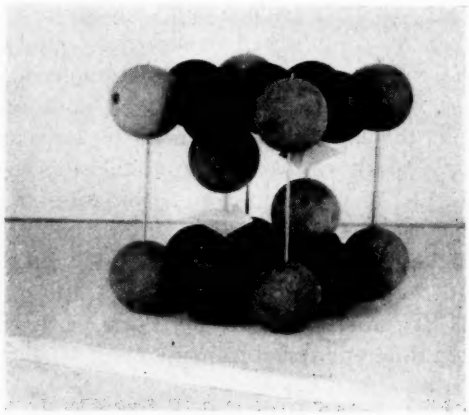

FIG. 1. Photograph of a model of the unit cell of $Cs_3As_2Cl_9$, with the chloride ions of layer A and all caesium ions shown as spheres in closest-packing. Positions of arsenic and of the chlorine atoms of layers B and C are indicated as the vertices of the triangular pyramids, which have the dimensions of structure II.

[4] See Astbury and Yardley, *Tabulated Data for the Examination of the 230 Space-groups by Homogeneous X-Rays*, Phil. Trans. **224**, 221–57 (1924).

[5] Linus Pauling, J. Am. Chem. Soc. **49**, 765 (1927).

[6] The value of the crystallographic rhombohedral angle α is incorrectly given by Groth, reference 1, as 89° 3′ instead of 90° 30′.

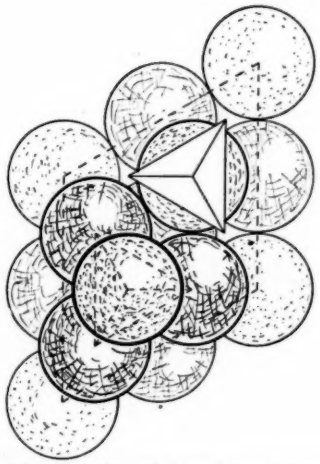

FIG. 2. Packing drawing of three layers parallel to (00·1) showing the undistorted closest-packed structure made up of spheres of the same size throughout. Caesium may be distinguished from chlorine atoms by the type of shading.

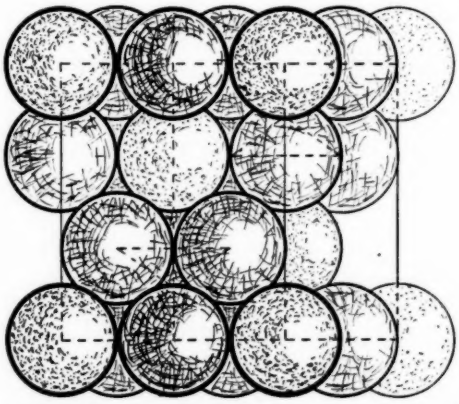

FIG. 3. Packing drawing of the unit cell normal to (10·0) with caesium and chlorine atoms shown as spheres in closest-packing. The positions of arsenic are indicated by the apices of the pyramids.

altogether likely that a suitable distortion of the ideal structure will account for all of the x-ray data.

Each chlorine of layer A is shared between two $AsCl_6$ octahedra, while each chlorine of layers B and C is a part of but one such group. Regarding the structure as a purely ionic aggregate of Cs^+, As^{+3}, and Cl^-, we see that the strength of the electrostatic valence (including the contribution of Cs^+) reaching each Cl^- of layer A is $2\frac{1}{6}$, while to each Cl^- of layers B and C it is $1\frac{5}{6}$. Actually we expect the arsenic to have a strong tendency to form three normal covalent bonds with chlorine, and the ionic model shows clearly that such bonds would be formed between arsenic and the chlorines of layers B and C; for the formation of such bonds means that arsenic layers will be found somewhat closer to layers B and C than they are to layer A. It appears also that the twofold axes are to be retained and that the actual structure is based upon D_3^2 or D_{3d}^3 rather than C_{3v}^1.

With either D_3^2 or D_{3d}^3, caesium and arsenic are placed in the following positions: Cs in 000, $\frac{1}{3}\frac{2}{3}u$, $\frac{2}{3}\frac{1}{3}\bar{u}$, As in $\frac{1}{3}\frac{2}{3}v$, $\frac{2}{3}\frac{1}{3}\bar{v}$. We expect $u \leqq \frac{1}{3}$, $\frac{2}{3} < v \lesssim \frac{5}{6}$. Moreover, the complete structure factor including chlorine for (00·l) reflections is identical for the two space-groups, namely

$$S_{(00.l)} = f_{Cs}(1+2\cos 2\pi lu) + 2f_{As}\cos 2\pi lv + 3f_{Cl}(1+2\cos 2\pi lz),$$

in which $z \leqq \frac{1}{3}$. We have intensity data for the first twelve orders of reflections from (00·1) with which to compare theoretical values for the proposed structure as calculated from the formula

$$I = C\frac{1+\cos^2 2\theta}{2\sin 2\theta} l|S|^2.$$

No corrections are included for extinction or for the decrease in intensity arising from the thermal vibrations of the atoms within the lattice. The f-values of Pauling and Sherman[7] are employed throughout this paper. The factor l is required since we are considering reflections at small angles from a thin plate-like but strongly absorbing crystal which was at all times completely bathed in radiation; the effective cross section of the beam was proportional then to sin θ and therefore to l. Estimating the mass absorption coefficient as about 40 for Mo $K\alpha$-radiation, we calculate that there would be only a quite negligible transmission except, perhaps, for the last two or three orders. Experimental intensities were estimated by visual comparison of reflections from a number of photographs with widely varying times of exposure with an intensity scale prepared for this use. The reflections become more diffuse as the order increases, and, as our considerations have to do with integrated intensities, it may be that we have somewhat underestimated the intensities of the last two or three reflections.

[7] Pauling and Sherman, Zeits. f. Krist. **81**, 1 (1932).

With the values of the parameters corresponding to closest-packing of Cs^+ and Cl^-, neither caesium nor chlorine would contribute to reflections with $l/3$ not integral. We do not find it possible to account for such reflections by considering them as due to arsenic alone, but rather that with $0.795 < v < 0.815$ and with both u and z slightly less than $\frac{1}{3}$, a general agreement is obtained between calculated and observed intensities. Table I contains these data for

TABLE I. *Comparison of calculated with observed intensities for (00·l) reflections.*
$u=0.320$, $v=0.805$, $z=0.325$

l	Observed intensity	Calculated intensity*	l	Observed intensity*	Calculated intensity*
1	8	8	7	0.5	5
2	25	25	8	6	28
3	150	250	9	8	93
4	4	13	10	4	41
5	0	1	11	0	4
6	75	195	12	1	32

* Temperature factor not included.

$v=0.805$, $u=0.320$, $z=0.325$, which values seem to be most satisfactory. As $3f_{Cl}$ is nearly equal to f_{Cs}, we see that the contributions of these two kinds of atoms are nearly identical in case $u=z$. It seems improbable that either u or z is less than 0.315, or that both together can be appreciably less than 0.320. However, it seems most satisfactory to have both u and z somewhat less than $\frac{1}{3}$. Making the caesium parameter slightly less than that for chlorine appears reasonable from a consideration of dimensional relations, but is otherwise quite arbitrary.

We now proceed to compare calculated intensities for $(h0\cdot0)$ and $(hh\cdot0)$ reflections with the experimental data. These data are the result of transmission photographs taken through the thin plates, which, however, were of such small diameter as to be completely bathed in radiation at all times. The intensity formula employed was identical in form with that already given except for the omission of the factor l. In this case the correction for absorption increases with the order, but calculation shows that the increase is not large enough at most to be very important.

The form of the structure factor depends upon the space-group of the structure. If it be based upon D_{3d}^3, all chlorine atoms lie in planes of symmetry and the structure has but one parameter at right angles to c; in particular, all atoms of layer A occupy no-parameter positions, and each caesium ion is surrounded by six equidistant chloride ions. If on the other hand the true space-group be D_3^2, the planes of symmetry are no longer retained, and three of these six chlorides could be nearer than the others to each caesium ion. This second possibility seems to us the more probable, especially in view of the fact that $Rb_3As_2Cl_9$ apparently is isomorphous with our compound, and the considerably smaller radius of 1.48A for Rb^+ as compared with 1.69A for Cs^+ and 1.81A for Cl^- would seem to require such a closer anion-cation approach. Six chlorine atoms would then occupy the general positions of D_3^2, and the chlorines of all layers could be rotated somewhat about the threefold axes away from the closest-packed positions for identical spheres, with probably a better distribution of structural strains than is obtainable from D_{3d}^3. We have then,

3 Cl in $w00$; $0w0$; $\bar{w}\bar{w}0$ with $w=0.480$,
6 Cl in x, y, z; $y-x, \bar{x}, z$; $\bar{y}, x-y, z$;
$y, x, \bar{z}$; $\bar{x}, y-x, \bar{z}$; $x-y, \bar{y}, \bar{z}$,

with $x \cong \frac{1}{3}$, $y \cong \frac{1}{6}$, $z=0.325$. If the structure were based on D_{3d}^3, $x=2y$, and $w=\frac{1}{2}$.

The amounts of the deviations of x, y and w from the closest-packed positions seems to be too small to have any large effects upon the calculated intensities. In Table II we give calculated intensities for structure I for which $x=\frac{1}{3}$, $y=\frac{1}{6}$, $w=\frac{1}{2}$ as well as for structure II based

TABLE II. *Comparison of calculated with observed intensities for (h0·0) and (hh·0) reflections.*
Structure I: $x=\frac{1}{3}$, $y=\frac{1}{6}$. Structure II: $x=0.365$, $y=0.200$.

$hk\cdot0$	Observed intensity	Calculated intensity* Structure I	Calculated intensity* Structure II
11·0	40	40	40
22·0	32	45	37
33·0	4	5.4	6.5
44·0	3	10.0	6.5
55·0	0	1.4	0.8
10·0	6	6	6
20·0	1	2.4	1.2
30·0	16	36	21
40·0	0	0.8	0.3
50·0	0	0.5	0.0
60·0	8	34	14

* Temperature factor not included.

upon D_3^2 for which $x=0.365$, $y=0.200$, $w=0.480$. The agreement is generally satisfactory in both cases, although somewhat better for the second. The data indicate that there is indeed some distortion from structure I, and that structure II is one variation which meets the intensity requirements. Table III contains some intensity comparisons which are representative of a more general type of reflection. The data are given only for structure II, but again the comparisons are appreciably better than for the undistorted structure. That we have arrived at essentially the correct structural type is scarcely to be doubted, but it is primarily upon the basis of dimensional and structural rather than intensity considerations that we decide that distortions from the ideal structure are to be introduced in accordance with D_3^2 rather than D_{3d}^3.

TABLE III. *Comparison for structure II of calculated with observed intensities for (0k·l) reflections.*

0k·l	Observed intensity	Calculated intensity*	0k·l	Observed intensity	Calculated intensity*
01·2	3	3.0	02·2	120	140
01·$\bar{2}$	40	47	02·$\bar{2}$	0	0.3
01·3	0	1.5	02·3	2	2
01·$\bar{3}$	0	0.1	02·$\bar{3}$	1	1.2
01·4	32	80	02·4	6	12
01·$\bar{4}$	8	20	02·$\bar{4}$	64	125
01·5	0	0.5	02·5	24	55
01·$\bar{5}$	2	5.5	02·$\bar{5}$	0	1.5
01·6	6	13	02·6	4	12
01·$\bar{6}$	2	5.5	02·$\bar{6}$	3	10
01·7	1	5.5	02·7	0	0.3
01·$\bar{7}$	0	0.5	02·$\bar{7}$	12	50
01·8	3	12	02·8	12	53
01·$\bar{8}$	2	9.2	02·$\bar{8}$	3	17

* Temperature factor not included.

DISCUSSION OF THE STRUCTURE

A photograph of a model of the structure is reproduced in Fig. 1. In this model the chloride ions of layer A and all caesium ions are shown as spheres of equal size in closest-packing, while the positions of arsenic atoms and of the chlorine atoms of layers B and C are indicated as the vertices of the triangular pyramids. Figs. 2 and 3 show packing drawings of the unit cell, again with caesium and chlorine atoms indicated as spheres of equal size in true closest-packed array, and with the positions of arsenic marked by the apices of the pyramids. Study of these drawings indicates the essential nature of the structure, and the process of going over to the parameters of structure II may then be visualized quite easily.

There are two factors which show that the plane $z=\frac{1}{2}$ between layers B and C should be a natural cleavage plane: (1) the absence of arsenic atoms in this region, and (2) the fact that both chlorine and caesium parameters along c are slightly less than $\frac{1}{3}$.

Since the basal plane intensities require $v=0.805\mp0.010$ rather than $\frac{5}{6}$, we see, as is indicated in the various figures, that arsenic trichloride molecules would seem to have their identity preserved within the structure, and that the process of crystallization has consisted in embedding $AsCl_3$ in an environment of completely ionized caesium chloride in such a manner that the large atoms or ions are in nearly closest-packing. The ratio of 3Cl per Cs, leading to the kind of layers already described, is particularly well suited to the requirements of this general type of structure. This ratio is also shown by the widely occurring perovskite or $KMgF_3$ structure.

We believe, moreover, that the size and shape of the $AsCl_3$ molecules are probably described well by structure II. Arsenic is expected to form three normal covalent bonds at angles somewhat greater than 90° but less than the tetrahedral angle.[8] Thus in elementary arsenic three bonds are formed at 97°, while electron diffraction

TABLE IV. *Interatomic distances calculated from structures I and II.* (The subscripts refer to the layers.)

Atom	Neighbors	Separation structure I	Separation structure II
As_v	$3Cl_C$	2.42A	2.25A
As_v	$3Cl_A$	2.75	2.76
Cs_A	$3Cl_A$	3.685	3.54
Cs_A	$3Cl_A$	3.685	3.83
Cs_A	$C3l_B$, $3Cl_C$	3.59	3.71
Cs_B	$3Cl_A$	3.55	3.56
Cs_B	$3Cl_C$	3.81	3.69
Cs_B	$3Cl_B$	3.69	3.57
Cs_B	$3Cl_B$	3.69	3.83
Cl_A	$4Cl_A$	3.685	3.70
Cl_A	Cl_B, Cl_C	3.59	3.55
Cl_A	Cl_B, Cl_C	3.59	3.55
Cl_B	$2Cl_B$	3.685	3.35
Cl_B	$2Cl_B$	3.685	4.04
Cl_B	Cl_C	3.78	3.78
Cl_B	Cl_C	3.78	4.08

[8] Linus Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).

studies[9] of $AsCl_3$ lead to $101\pm4°$ bond angles. An As−Cl separation of 2.18 ± 0.03A is given by the electron diffraction study, while a value of 2.20A is obtained from Pauling and Huggins' covalent radii.[10] Structure II, which has $v=\mp0.805$, $x=0.365$, $y=0.200$, $z=0.325$, contains $AsCl_3$ molecules with bond angle 95°50′, As−Cl $=2.25$A, Cl−Cl$=3.34$A. Table IV lists all of the pertinent interatomic distances for the two structures for which we have calculated intensities. The As−Cl separation of 2.25A given by structure II is nearly that expected for a covalent bond, whereas the precise significance of the corresponding value of 2.42A given by structure I would remain doubtful. Moreover the relations of caesium with chlorine are probably more satisfactory in general for structure II than for structure I.

Possible variations in the parameter values would include having z about 0.005 smaller, v from 0.005–0.010 smaller, and x and y a little nearer the closest-packed positions. Such changes would not materially alter our concept of covalent As−Cl bonds, but would lead to bond angles a little greater than 96°. They would result also in a somewhat smaller value than 3.71A for the Cs_A-Cl_B distance, which is perhaps to be anticipated.

[9] Brockway and Wall, J. Am. Chem. Soc. **56**, 2373 (1934).
[10] Pauling and Huggins, Zeits. f. Krist. **87**, 205 (1934).

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On the Two-Quantum Σ-States of the Hydrogen Molecule

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A wave function in the form of a series with coefficients to be determined by the variational method is used to calculate the dissociation energies of the hydrogen molecule in two of its excited states: $1s\sigma 2s\sigma\ {}^3\Sigma_g^+$ and $1s\sigma 2p\sigma\ {}^1\Sigma_u^+$. In the former case an 11-term wave function gives an energy less than 0.02 e.v. from the most probable experimental value and lying within the limits of experimental error. For the second state an energy less than 0.08 e.v. from experiment is obtained by means of a function comprising 18 terms. The interelectronic distance has been introduced explicitly into the wave function and the role that it plays in reducing the energy is discussed at length. The limits of accuracy of the calculation with reference to convergence and nuclear motion are considered. Explicit wave functions are given for the two states.

INTRODUCTION

THE treatment by wave mechanics of the electronic states of a diatomic molecule has led in general to results which are unsatisfactory from a quantitative point of view. The very simplest problems, including the excited states of the hydrogen molecule, have not been carried to the point where quantitative agreement with experiment could be obtained. The successful treatment of the normal state of the hydrogen molecule by James and Coolidge[1] furnishes a method whose possibilities it seems worth while to explore more thoroughly; and with this in mind a calculation has been made on several of the two quantum states of hydrogen,[2] and the results for two of these states are reported in this paper.[3]

Previous work on these states has been based on trial wave functions that have been constructed from hydrogen atom functions[4] (cf. the Heitler-London method), from the wave functions for the hydrogen molecular ion,[5] or from a combination of the two.[6] In a molecule as closely

[1] James and Coolidge, J. Chem. Phys. **1**, 825 (1933).
[2] Two-quantum molecular states dissociate upon adiabatic separation of the nuclei into one normal atom and one atom in a two-quantum state.
[3] Work has also been done on the repulsive state $1s\sigma 2p\sigma\ {}^3\Sigma_u^+$ and will be published shortly in a joint paper by Drs. James and Coolidge with the writer.
[4] Kemble and Zener, Phys. Rev. **33**, 512 (1929); Zener and Guillemin, Phys. Rev. **34**, 999 (1929).
[5] E. A. Hylleraas, Zeits. f. Physik **71**, 739 (1931). Hylleraas fails to treat the state $1s\sigma 2s\sigma\ {}^3\Sigma_g^+$, but mentions results obtained by a rough extrapolation which appears to have little theoretical justification.
[6] J. K. L. MacDonald, Proc. Roy. Soc. **A136**, 528 (1932). MacDonald treats all of the two-quantum states for the same internuclear distance, 2 Bohr radii. Both Hylleraas and MacDonald obtain fairly good agreement with experiment on the Π states, but their results on the Σ states are unsatisfactory.

bound as hydrogen it is to be expected that the molecular ion function of Hylleraas and the hybrid function of MacDonald will be more effective than a Heitler-London function, as is confirmed by their results. However these wave functions, together with all others previously employed, suffer a twofold disadvantage which renders them unsatisfactory if accurate results are desired: (1) they are insufficiently flexible, if flexible at all; (2) they take no adequate account of electronic interaction; e.g., for Σ states they are functions of only four of the five essential coordinates, the interelectronic distance or its equivalent having been omitted.

The importance of taking account of electronic interaction in the wave function is to ensure that there will be a small probability for those regions of configuration space in which the electrons are close together. For example, the introduction of positive powers of the interelectronic distance (r_{12}-terms) into the wave function will serve to keep the electrons apart, and where that service is partly accounted for by other means, r_{12}-terms will be less important. Thus r_{12}-terms should be less important for triplet than for singlet states, since the wave function for a triplet state is antisymmetric in the space coordinates of the electrons and will vanish when they coincide. Also the explicit appearance of azimuthal angles in the wave function for a Π state will compensate in some measure for the absence of r_{12}-terms, if the state happens to be a triplet. In consequence we should expect that functions of the type previously used would have given somewhat better agreement for triplet than for singlet states and better for $^3\Pi$ than for $^3\Sigma$. This appears to be in agreement with the results of MacDonald, although the former effect is not so marked as one might suppose. A more detailed discussion of some of these points is reserved till later when a comparison can be made with the results of the present work.

Method

The observed two-quantum Σ states are $1s\sigma 2s\sigma\ ^3\Sigma_g^+$ (the most probable upper state for the continuous spectrum), $1s\sigma 2p\sigma\ ^1\Sigma_u^+$ (the B state) and $1s\sigma 2p\sigma\ ^3\Sigma_u^+$ (the Heitler-London repulsive state). The symmetry characteristics impose two types of conditions on the wave functions:

(1) Symmetry or antisymmetry to interchange of the space coordinates of the electrons (singlet or triplet states).

(2) Symmetry or antisymmetry to interchange of the space coordinates of the nuclei (even (g) or odd (u) positive electronic states).[7] Furthermore the wave function of a Σ state must have rotational symmetry about the nuclear axis and can contain only the difference between the azimuthal angles of the electrons.

It is proposed to expand the wave function in terms of a power series in the five variables with an exponential factor in the elliptical coordinate λ to ensure convergence of the integrals involved. If the nuclei are designated by a and b and the electrons by 1 and 2, and the distances between the particles expressed in Bohr radii (B.R.) are denoted by the customary symbols, then the coordinates are:

$$\lambda_1=(r_{1a}+r_{1b})/R, \quad \lambda_2=(r_{2a}+r_{2b})/R,$$

$$\mu_1=(r_{1a}-r_{1b})/R, \quad \mu_2=(r_{2a}-r_{2b})/R, \quad \rho=2r_{12}/R.$$

The wave function is:

$$\psi=\sum_{mnjkp} c_{mnjkp}[m\delta_1 n\delta_2 jkp],$$

where $[m\delta_1 n\delta_2 jkp]$ stands for

$$(1/2\pi)\{e^{-\delta_1\lambda_1-\delta_2\lambda_2}\lambda_1^m\lambda_2^n\mu_1^j\mu_2^k\rho^p \pm e^{-\delta_2\lambda_1-\delta_1\lambda_2}\lambda_1^n\lambda_2^m\mu_1^k\mu_2^j\rho^p\}.$$

No spin function is introduced, but the spin is determined implicitly by the symmetry characteristics of the wave function ψ in accordance with Pauli's principle. For singlet states the plus sign is to be used, for triplet states the minus sign. For the even (g) states $j+k$ must be even, for the odd (u) states odd. Subject to this last restriction the summation is to be extended over positive or zero values of the indices and as many terms taken as result in an effective lowering of the energy. The quantities δ_1 and δ_2 should preferably be taken as arbitrary parameters to be varied, but since there appeared to

[7] Σ^+ terms are $\frac{\text{symmetric}}{\text{antisymmetric}}$ in the space coordinates of the nuclei if they are $\frac{\text{even}(g)}{\text{odd}(u)}$.

be no simple way of performing this variation, suitable values were selected at the outset of the calculation by a preliminary computation described below. A small error in the choice of δ_1 and δ_2 should be compensated for by a slight alteration in the coefficients of terms involving powers of λ_1 and λ_2. The best values of these constants will depend on the internuclear distance R, and a particular choice of δ's will give reasonably good results over a small range in R.[1] The electronic energy plotted as a function of R will be the envelope of a family of curves characterized by different pairs of values of the parameters δ_1 and δ_2 such that each pair of values will be the best for that particular R at which its curve touches the envelope.

The variational method was applied to determine a set of values for the parameters c_{mnjkp} which would give the lowest energy obtainable with the type of function used. Since only the lowest states of a particular symmetry are considered, the computed value of the energy for any trial function must always lie above the true energy. The actual computation falls naturally into three parts. In the first, extensive tables of fundamental integrals, related by convenient recursion formulas, are prepared for use in evaluating the matrix elements of the successive approximations. The principal labor occurs in the integrations over $1/r_{12}$, which is expanded by the Neumann formula, and in the evaluation of integrals between r_{12}-terms. In the second part the matrix elements corresponding to combinations of the simplest terms in the series, are evaluated and introduced into the secular equation. If the parameters δ_1 and δ_2 are approximately correct, it is found that the series converges rapidly and that only low powers (0, 1, 2 but never more than 3) are required. Since in the nth approximation there are $n(n+1)/2$ matrix elements to be computed and a secular equation of the nth degree to be solved, it is not feasible to test every term in combination with all the others nor to carry along any terms which give inappreciable contributions. As the importance of any term was generally found to decrease as the number of terms combined with it was increased, terms which yielded negligible improvement at any stage of the calculation were usually dropped. However, exceptions have been found to this rule, notably in the case of certain pairs of functions, e.g. $[0\delta_1 0\delta_2 000]$ and $[1\delta_1 1\delta_2 000]$ in treating $^3\Sigma_g^+$ which gave in combination a better contribution to the energy than the sum of their individual contributions when inserted independently. This phenomenon, which is fortunately infrequent in occurrence, seems to indicate that the δ's have not exactly the right values to ensure the closest convergence.

The third part of the work consists in the solution of the secular equations which arise in each approximation. The procedure is necessarily one of trial and error and involves the evaluation of large numbers of symmetric determinants.[1] Here there were no neighboring electronic states of the same symmetry, i.e., no nearby roots of the secular equation, and it was found sufficiently accurate to interpolate linearly for λ, the value of the root. The coefficients of the wave function are readily obtained from a secular determinant evaluated at the root. Before working out this determinant it is desirable to rearrange the terms by putting an important function at the end to ensure that the last factor of the determinant will reduce to a vanishingly small quantity.

The State $1s\sigma 2s\sigma\ ^3\Sigma_g^+$

In order to make use of tables already prepared[1] in treating the normal state of the molecule, computations were begun on the state $1s\sigma 2s\sigma\ ^3\Sigma_g^+$ with a wave function for which $\delta_1=\delta_2=0.75$. It was soon found that the convergence was extremely poor, and this was attributed to an unfavorable choice of shielding constants. Thereupon a preliminary investigation for determining a suitable pair of δ's was made upon the single term $[1\delta_1 0\delta_2 000]$ which in the previous work had proved to be the most important single term of the series; this led to the selection of $\delta_1=0.5$ $\delta_2=1$ for treating this state of the molecule. The calculation was then carried out for the internuclear distance $R=1.87$ B.R. at which occurs the minimum of the experimentally determined potential energy curve.[8]

[8] It would have been more convincing to have established this also as the theoretical minimum. However it is well known that the experimentally determined Morse curves are quantitatively accurate in the neighborhood of the minimum.

The six terms [10020] [10200] [10000] [00000] [10110] [11000][9] were found to give an energy much better than any previously reported,[10] less than 0.08 e.v. from experiment. Upon the insertion of r_{12} terms the energy was still further reduced and the final wave function involving [10020] [10200] [10000] [00000] [10110] [11000] [11020] [10001] [00001] [10021] [11001] gave a total energy of -0.7361 in units of twice the ionization energy of the normal hydrogen atom: $2R_\infty hc$ (27.074 e.v.). A number of other terms were investigated at various stages of the calculation including: [20000] [01000] [11200] [10130] [12000] [11110] [10111]; these were all found to yield 0.001 e.v. or less. The r_{12} terms contributed 0.057 e.v. in marked contrast to the improvement of 0.44 e.v. observed in the ground state (singlet) by James and Coolidge; this difference is easily understandable from the orbital antisymmetry of the triplet state. Because of the extremely rapid convergence it was possible to make an estimate of the probable contribution of remaining terms, from which the absolute minimum may be said to occur at $\lambda=-0.7367\pm0.0004(-19.945\pm0.01$ e.v.). Subtracting the zero point energy of 0.162 e.v. and the energy -16.921 e.v. of a normal and a two-quantum hydrogen atom (with fixed nuclei), we obtain 2.862 ± 0.01 e.v. for the dissociation energy of the hydrogen molecule in the state $1s\sigma 2s\sigma\ {}^3\Sigma_g^+$. The experimental value is given by Richardson as 2.867 e.v., by Mulliken as 2.86 e.v. and by Jevons as 2.85 e.v.[11]

The unusual degree of accuracy which has been obtained for this state makes it necessary for us to consider closely the approximation which has been made in the customary assumption of "clamped nuclei." The correction to the energy for Σ states may be roughly estimated by means of the limiting case of the united atom. The electronic energy[12] is then effectively raised by an amount:[13, 14]

$$\bar{U}=\frac{h^2}{8\pi^2\mu}\left[\frac{L(L+1)}{R^2}+\sum_{\text{spin}}\int\left(\frac{\partial\Phi}{\partial R}\right)^2 d\tau_{\text{elec.}}\right],$$

where μ is the reduced mass of the molecule, L the resultant orbital angular momentum of the united atom and Φ the electronic part of the wave function. Since this expression is always positive it appears that the uncorrected electronic energy may lie below the experimental value. A consideration of the effect of nuclear motion in Hylleraas' very exact calculation on parahelium[15] led to a similar result. For the state under consideration ($1s\sigma 2s\sigma\ {}^3\Sigma_g^+$) the first term in $\bar{U}$ will vanish. It would seem to be a matter of considerable difficulty to appraise the second term; fortunately this has been done by MacDonald[6] who finds it to be worth about 0.01 e.v. The minimum of the corrected potential energy curve will therefore occur at $\lambda=-19.935\pm0.01$ e.v. However, since corrections have now been made for nuclear motion, we must subtract the true value of the two-quantum asymptote (-16.912) and this leaves us with nearly the same dissociation energy as before: 2.861 ± 0.01 e.v. The approximations made in assuming the minimum of the experimentally-determined potential energy curve to be the true minimum, in estimating the convergence of the series wave function and in correcting for the effect of nuclear motion take us into a region of accuracy where spin and relativistic effects can no longer be neglected.

The State $1s\sigma 2p\sigma\ {}^1\Sigma_u^+$

Next to be treated was the B state $1s\sigma 2p\sigma\ {}^1\Sigma_u^+$. In order to secure the best results, it would have been advisable to have adopted the same procedure for determining δ_1 and δ_2 as that employed in the preceding work, but this would have necessitated the entire recalculation of all the tables of fundamental integrals from the very beginning. The calculation was therefore carried out with $\delta_1=0.5$, $\delta_2=1$ at the Morse curve minimum $R=2.42$ B.R. A great many terms were tried and it was found that few could be rejected. A wave function comprising the terms [10010] [10100] [11100] [00100] [11010] [10120] [20100] [01100] [00300] [02100] [01120] [01300] [11120] [00101] [10101]

[9] $[m\delta_1 n\delta_2 jkp]$ is abbreviated to $[mnjkp]$ for $\delta_1=0.5$, $\delta_2=1$.

[10] MacDonald's result is 0.40 e.v. from experiment.

[11] O. W. Richardson, *Molecular Hydrogen and Its Spectrum*, p. 324; R. S. Mulliken, Rev. Mod. Phys. **4**, 78 (1932); W. Jevons, *Report on Band Spectra of Diatomic Molecules*, p. 268.

[12] "Electronic" energy includes energy of nuclear repulsion.

[13] R. de L. Kronig, *Band Spectra and Molecular Structure*, pp. 14, 15.

[14] R. de L. Kronig, Physica **1**, 7 (1934).

[15] E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929).

[11101] [01101] [10121] gave the best energy of -0.7522 (-20.37 e.v.) which is approximately 0.08 e.v. from the experimental value given by Mulliken.[16] The addition of r_{12} terms to the wave function lowered the energy by 0.29 e.v. The slowness of convergence is undoubtedly to be attributed primarily to the fact that δ_1 and δ_2 have not been given their best values. Since the r_{12} terms are quite important and since they were inserted last in order, it might be thought that if they had been put in somewhat earlier, several of the non-r_{12} terms would have proved to be less important and might even have been dropped altogether. The contribution of some of these terms was noticeably decreased, but it appears that none of the 18 could have been omitted without sacrificing 0.01 e.v. or more, e.g., the best 15-term wave function, whose coefficients are given in Table I, gave an energy worse by 0.06 e.v. In estimating the convergence of remaining terms, the greatest error appears to be due to the absence of those with higher powers of r_{12}. In the treatment of the normal state these terms proved to be worth about one-sixth of the energy contributed by the first power terms. Allowing from 0.04 to 0.06 e.v. for this purpose and, upon examination, from 0.01 to 0.05 e.v. for convergence of other terms, one obtains 3.44 ± 0.03 e.v. for the dissociation energy of the B state, as compared with the values 3.42, 3.44 and 3.47 e.v. given by Richardson, Mulliken and Jevons, respectively. This estimate is not quite so reliable as that made on the state $^3\Sigma_g^+$.

Relative to the total energy, the r_{12} terms in the B state are of the same order of importance as in the ground state. Thus it is clear that the greater importance of the r_{12} terms for these two states is to be attributed almost entirely to the fact that they are both singlets. One might suppose that there would be less overlapping of the electron orbits in a two-quantum state than in the normal state, and that r_{12} terms would be correspondingly less important in the former case. Thus Hylleraas and Undheim[17] find that for two-quantum para-helium the r_{12} terms contribute only one-tenth as much to the energy as in the ground state. The situation in the molecule is sufficiently different from that in the atom to make understandable the fact that the r_{12} terms do not drop off in importance in the molecule to the extent that they do in the atom as one passes from the ground state to the excited levels.[18]

[16] The energies calculated by Hylleraas and MacDonald are, respectively, 0.25 and 0.50 e.v. from experiment.

[17] Hylleraas and Undheim, Zeits. f. Physik **65**, 759 (1930).

Concluding Remarks

The best wave function for the state $^3\Sigma_g^+$ and the best 15-term wave function for the B state are given in Table I. A recalculation of the latter state with a specially selected pair of δ's would probably reduce the number of terms considerably and provide a somewhat lower value of the energy. A preliminary examination of the term $[0\delta_1 0\delta_2 100]$ for a range of values of δ_1 and δ_2 should enable one to select a suitable pair, or else one might determine δ_1 and δ_2 by requiring a simpler function to approximate the function given in Table I or a certain number of its more important terms. Tables of matrix elements for combinations of numerous terms have been pre-

Table I. *Coefficients of the normalized* wave functions* (c_{mnjkp}).

$^3\Sigma_g^+(\lambda=-0.73609,\ R=1.87)$		$^1\Sigma_u^+(\lambda=-0.74986,\ R=2.42)$	
[00000]	−1.161959	[00100]	1.441073
[10000]	0.499368	[10100]	−0.231754
[11000]	−0.077834	[10010]	0.002751
[10110]	−0.014422	[01100]	−0.560549
[10020]	0.071975	[11100]	0.007094
[10200]	0.034815	[11010]	−0.009393
[11020]	−0.018709	[20100]	0.019232
[00001]	0.091777	[10120]	0.207040
[10001]	−0.004742	[02100]	0.077989
[11001]	−0.000503	[01120]	−0.106513
[10021]	0.009030	[00300]	0.096702
		[00101]	0.210583
		[10101]	−0.016744
		[01101]	−0.020524
		[10121]	−0.014764

* Note the factor $1/2\pi$ in the wave function.

[18] In the two-quantum atom the inner electron will be moving rapidly with respect to the outer electron in a smaller orbit. Classically speaking, its motion could then be represented by a spherical cloud of charge shielding the nucleus (the shielding for two-quantum para-helium is 80 percent effective). The interaction of the outer electron with this charge cloud is a function only of its distance from the center, i.e., the nucleus, so that r_{12}-terms will not be needed to describe the motion. On the other hand in the excited molecule the electrons will have lost their one-and two-quantum atomic characteristics to a large extent (all the more so for a closely bound molecule such as hydrogen), and will move with more nearly equal velocities in much the same region of space between the nuclei. Thus r_{12}-terms will be nearly as important as in the ground state.

pared for treating both even (g) and odd (u) states. These tables, although unpublished, are accessible and may be used for calculating any of the 3-quantum Σ states or the unobserved state $1s\sigma 2s\sigma\ {}^1\Sigma_g{}^+$. These states should appear as higher roots of the secular determinants, for to each higher root there will correspond a state of the system such that the nth lowest root will be an upper limit for the energy of the nth lowest state of the given symmetry.[17]

In possible extensions of the James-Coolidge method to other molecules, the present work would indicate that where it becomes a practical impossibility to take into account r_{12} terms or their equivalent, quantitative results for Σ states can be expected only if the states are antisymmetrical in the space coordinates of all the electrons.[19]

In conclusion I wish to thank Dr. H. M. James and Dr. A. S. Coolidge for the use of their tables, and I am especially indebted to Dr. James for valuable advice and encouragement. I am also obliged to Professor Kemble for helpful comment on the manuscript.

Appendix

The procedure adopted for evaluating the matrix elements follows closely that described in the appendix of James and Coolidge, and will consequently not be reproduced in detail. Modifications of most of the formulas are needed because the previous work was restricted to the special case $\delta_1=\delta_2$.

The required quantities can all be found in terms of the integrals:

$$X(m\alpha_1 n\alpha_2 jkp)=\frac{1}{4\pi^2}\int\int\int\int\int\int(\lambda_1{}^2-\mu_1{}^2)e^{-2\delta_1\lambda_1-2\delta_2\lambda_2}\lambda_1{}^m\lambda_2{}^n\mu_1{}^j\mu_2{}^k\rho^p d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2,$$

$$X(m\alpha_2 n\alpha_1 jkp)=\frac{1}{4\pi^2}\int\int\int\int\int\int(\lambda_1{}^2-\mu_1{}^2)e^{-2\delta_2\lambda_1-2\delta_1\lambda_2}\lambda_1{}^m\lambda_2{}^n\mu_1{}^j\mu_2{}^k\rho^p d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2,$$

$$X(m\alpha n\alpha jkp)=\frac{1}{4\pi^2}\int\int\int\int\int\int(\lambda_1{}^2-\mu_1{}^2)e^{-(\delta_1+\delta_2)(\lambda_1+\lambda_2)}\lambda_1{}^m\lambda_2{}^n\mu_1{}^j\mu_2{}^k\rho^p d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2,$$

where $\alpha_1=2\delta_1,\ \alpha_2=2\delta_2,\ \alpha=\delta_1+\delta_2$.

The indices are all positive or zero except p which may have the value -1.

Consider the matrix component of unity between the two terms $[m_a\delta_1 n_a\delta_2 j_a k_a p_a]$ and $[m_b\delta_1 n_b\delta_2 j_b k_b p_b]$. Since each term is the sum or difference of two parts which we may designate ψ_a', ψ_a'' and ψ_b', ψ_b'', respectively, the matrix component of unity will have four parts:

$$S_{ab}=\int\int\psi_a'\psi_b' d\tau_1 d\tau_2+\int\int\psi_a''\psi_b'' d\tau_1 d\tau_2\pm\int\int\psi_a'\psi_b'' d\tau_1 d\tau_2\pm\int\int\psi_a''\psi_b' d\tau_1 d\tau_2,$$

where the plus sign is for singlet and the minus sign for triplet states. Remembering that

$$d\tau_1 d\tau_2=\frac{R^6}{64}(\lambda_1{}^2-\mu_1{}^2)(\lambda_2{}^2-\mu_2{}^2)d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2$$

we find:

$$S_{ab}=\frac{R^6}{64}\{2[X(m_a+m_b,\ \alpha_1,\ n_a+n_b+2,\ \alpha_2,\ j_a+j_b,\ k_a+k_b,\ p_a+p_b)$$
$$-X(m_a+m_b,\ \alpha_1,\ n_a+n_b,\ \alpha_2,\ j_a+j_b,\ k_a+k_b+2,\ p_a+p_b)]$$
$$\pm 2[X(m_a+n_b,\ \alpha,\ n_a+m_b+2,\ \alpha,\ j_a+k_b,\ k_a+j_b,\ p_a+p_b)$$
$$-X(m_a+n_b,\ \alpha,\ n_a+m_b,\ \alpha,\ j_a+k_b,\ k_a+j_b+2,\ p_a+p_b)]\}.$$

[19] Or at least in the space coordinates of the binding electrons.

The matrix component of the Hamiltonian energy will similarly consist of four parts:

$$H_{ab}=I\begin{pmatrix}m_a\delta_1 n_a\delta_2 j_a k_a p_a\\ m_b\delta_1 n_b\delta_2 j_b k_b p_b\end{pmatrix}+I\begin{pmatrix}n_a\delta_2 m_a\delta_1 k_a i_a p_a\\ n_b\delta_2 m_b\delta_1 k_b j_b p_b\end{pmatrix}\pm I\begin{pmatrix}m_a\delta_1 n_a\delta_2 j_a k_a p_a\\ n_b\delta_2 m_b\delta_1 k_b j_b p_b\end{pmatrix}\pm I\begin{pmatrix}n_a\delta_2 m_a\delta_1 k_a j_a p_a\\ m_b\delta_1 n_b\delta_2 j_b k_b p_b\end{pmatrix}.$$

The I's may be evaluated in terms of the X's by means of the following general formula:

$$\begin{aligned}I\begin{pmatrix}a\gamma_1 c\gamma_3 e g p_a\\ b\gamma_2 d\gamma_4 f h p_b\end{pmatrix}=\frac{R^4}{64}\Big\{&R\{X(02000)-X(00020)-8X(01000)+2X(0200-1)-2X(0002-1)\}\\&-4\{(d^2+d-h^2-h-\gamma_4{}^2)X(00000)-2\gamma_4(1+d)X(01000)+\gamma_4{}^2X(02000)+2\gamma_4 dX(0-1000)\\&-d(d-1)X(0-2000)+h(h-1)X(000-20)\}-4p_b\{(d-h)X(00000)-\gamma_4X(01000)\\&+(d+h+p_b+1)[X(0200-2)-X(0002-2)]+(h-d)[X(2000-2)+X(0020-2)]\\&+\gamma_4[X(2100-2)-X(0300-2)+X(0120-2)+X(0102-2)-2X(1011-2)]\\&+2dX(1-111-2)-2hX(111-1-2)\}\Big\}.\end{aligned}$$

The abbreviation $X(rstuv)$ has here been used for the integral

$$X(a+b+r,\ \gamma_1+\gamma_2,\ c+d+s,\ \gamma_3+\gamma_4,\ e+f+t,\ g+h+u,\ p_a+p_b+v).$$

Fortunately, by virtue of the unsymmetrical nature of this formula, the bracket multiplied by p_b will drop out for all combinations of non-r_{12} terms and for all combinations of an r_{12}-term with a non-r_{12} term.

The X's may all be evaluated in terms of generalized Z's by the following formulae:

$$X(m\alpha_1 n\alpha_2 jkp)=Z^0(m+2,\ \alpha_1,\ n,\ \alpha_2,\ j,\ k,\ p)-Z^0(m,\ \alpha_1,\ n,\ \alpha_2,\ j+2,\ k,\ p)$$

$$Z^\nu(m\alpha_1 n\alpha_2 jkp)=\frac{1}{4\pi^2}\int\int\int\int\int\int e^{-\alpha_1\lambda_1-\alpha_2\lambda_2}\lambda_1{}^m\lambda_2{}^n\mu_1{}^j\mu_2{}^k\rho^p M^\nu\cos^\nu(\varphi_1-\varphi_2)d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2,$$

$$M^2=(\lambda_1{}^2-1)(\lambda_2{}^2-1)(1-\mu_1{}^2)(1-\mu_2{}^2).$$

For the calculation of the Z's there are needed the generalized integrals $H_\tau{}^\nu(m\alpha_1 n\alpha_2)$ and $S(m\alpha_1 n\alpha_2)$, already familiar in molecular problems for the special case $\alpha_1=\alpha_2$. The details of these generalizations are more or less obvious and the relevant formulae[20] and recurrence relations may be obtained from the appendix of the James-Coolidge paper if one makes the following alteration in their formulae: replace the single α by α_1 and α_2 in such a way that m always goes with α_1 and n with α_2. For example:

$$Z(m\alpha_1 n\alpha_2 jk0)=4A_m(\alpha_1)A_n(\alpha_2)/(j+1)(k+1),$$

$$Z(m\alpha_1 n\alpha_2 jk-1)=\sum_{\tau=0}^{\infty}(2\tau+1)R_\tau(j)R_\tau(k)H_\tau(m\alpha_1 n\alpha_2),$$

$$H_1(m\alpha_1 n\alpha_2)=H_0(m+1,\ \alpha_1,\ n+1,\ \alpha_2)-S(m,\ \alpha_1,\ n+1,\ \alpha_2)-S(n,\ \alpha_2,\ m+1,\ \alpha_1).$$

[20] Some of these formulae are contained in a recent paper by H. M. James, J. Chem. Phys. **2**, 794 (1934).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Fractionation of the Oxygen Isotopes in an Exchange Reaction

Recently Urey and Greiff[1] have presented theoretical calculations on the equilibrium constants of exchange reactions involving the isotopes of the lighter elements and among others the exchange reaction,

$$2H_2O^{18}+CO_2^{16}=2H_2O^{16}+CO_2^{18}.$$

At 0°C the equilibrium constant for this reaction is found to be 1.097, which gives for the fractionation factor for this reaction 1.047, the O^{18} being concentrated in the carbon dioxide. This reaction is well suited to the separation of the oxygen isotopes by using counter-current scrubbing apparatus similar to fractionation columns in construction.

In this note we wish to report the experimental confirmation of the fractionation factor calculated from theory. The method consisted in passing carbon dioxide gas from a tank through three spiral wash bottles in series containing water from which the deuterium had been largely removed. The gas was then mixed with deuterium-free hydrogen gas prepared electrolytically and the mixture passed over a supported nickel catalyst to convert the carbon dioxide to methane and water. The specific gravity of the water in the wash bottles and the water produced catalytically from the carbon dioxide were compared. The deuterium-free water used in these experiments was prepared by electrolyzing a large volume of ordinary water, collecting the first 10 percent electrolyzed, then re-electrolyzing this and catching the first 10 percent re-electrolyzed. The fractionation factor of these cells runs between 9 and 10 and hence most of the deuterium should have been removed. The specific gravity of the water at 25° was 0.999979, determined with a pycnometer.* The specific gravities of the water from the wash bottles and from the carbon dioxide were compared by a pressure float method described by Gilfillan.[2] The determination of the specific gravity of the water from the wash bottles by this method agreed with the pycnometer value given above. Three determinations of the specific gravity of the water from the carbon dioxide gave a mean value for the specific gravity of 0.9999892, giving a difference in the two specific gravities of 10.2 parts per million with an error of not over 1 part per million. The calculated difference in density is 10.3 parts per million using 1.047 as the fractionation factor. The difference between these two values is within the experimental limit of error and also the probable error in the calculations as estimated by Urey and Greiff.

We are at present constructing a counter-current scrubbing apparatus with the object of separating the oxygen isotopes by the method outlined by these authors.

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January 16, 1935.

[1] Urey and Greiff, J. Am. Chem. Soc. **57**, in press (January, 1935).
[2] Gilfillan, J. Am. Chem. Soc. **56**, 406 (1934).
* This water was kindly prepared for us by Dr. W. G. Brown and A. F. Daggett, who will describe their plant in a forthcoming publication.

A Correction and Addition to the Discussion of the Ground State of H_2

Our recent paper[1] on the ground state of H_2 contains a minute error, detected on the eve of publication, about which we wish to make a more complete statement. When correctly computed the energies corresponding to the wave functions defined in that paper come out lower than the values there given by 0.003 e.v. for the 11-term function and by 0.001 e.v. for the 13-term function at the equilibrium distance. Furthermore, the functions are not accurately normalized; they should be reduced by approximately 0.05 percent, or the corresponding correction applied to the result of any calculation based on their published form. The 5-term function and the corresponding energy value were not affected by the error. In principle, it would be possible to improve the functions (aside from the question of normalization) by revising the ratios of the coefficients, but we have not undertaken this, as it is clear that the resulting improvement would be quite negligible.

The largest binding energy computed was -4.698 e.v. Correcting this by 0.006 ± 0.003 e.v. for the effect of nuclear motion,[2] and making an allowance of -0.03 ± 0.01 e.v.[3] for the improvement available from the addition of other terms, we get -4.722 ± 0.013 e.v. as the binding

energy of H_2 at the potential minimum. Correcting for the zero point vibration we then obtain for the dissociation energy of $H_2D_{H_2}=4.454\pm0.013$ e.v., as the probable result of a complete theoretical treatment of the problem.

We should like to mention also an unsuccessful attempt to improve our method by the introduction of the Wang function as a term in the series. For larger separations of the nuclei this would certainly be helpful, but for those under consideration this was not the case. The computations became somewhat more complicated through loss of uniformity in character, and no results were obtained on introduction of this function which could not be duplicated by the addition in its place of one or two terms of the standard form.

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January 14, 1935.

[1] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).
[2] A first order correction for this effect entered our work through the comparison of the fixed nucleus problem for both molecule and atoms.
[3] This differs from our previous estimate, which was -0.03 ± 0.02 e.v. An example of the method used in estimating convergence is contained in a paper on the $1s\sigma 2p\sigma\ ^3\Sigma_u$ state, now in preparation.